PB-217 156

FWPCA METHODS FOR CHEMICAL ANALYSIS OF WATER AND WASTES

Federal Water Pollution Control Administration
Cincinnati, Ohio

November 1969

DISTRIBUTED BY:

NTIS
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

210

PB 217 156

Federal Water Pollution Control Administration
Division of Water Quality Research
Analytical Quality Control Laboratory
Cincinnati, Ohio

CLEAN
WATER

FWPCA METHODS FOR CHEMICAL ANALYSIS OF WATER AND WASTES

NOVEMBER, 1969

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

MARCH 3, 1849

U.S. DEPARTMENT OF THE INTERIOR

24

PREFACE

→The This manual describes the analytical procedures selected for use
Federal Water Pollution Control Administration
in FWPCA laboratories for the chemical analysis of water and waste samples. The methods were chosen by a committee of senior chemists from within the Administration, using Standard Methods for the Examination of Water and Wastewater, 12th Edition (1965) and ASTM Standards, Part 23, Water; Atmospheric Analysis (1968) as basic references. Where acceptable methods were not available from these sources, detailed descriptions of suitable procedures are included in this manual.

In order to provide reliable water quality and waste constituent data for use by FWPCA, these procedures will be used in all Administration laboratories except under very unusual circumstances. Other agencies and individuals are encouraged to use these methods, in the interest of uniformity throughout the water pollution control effort.

David S Stephan
David G. Stephan
Assistant Commissioner
Research & Development

Allan Hirsch
Allan Hirsch
Acting Assistant Commissioner
Office of Operations

i

INTRODUCTION

This 1969 edition of "FWPCA Methods for Chemical Analysis of Water and Wastes" describes chemical analytical procedures to be used in FWPCA laboratories. The methods were selected by a team of senior scientists within FWPCA based on the following criteria:

(1) The method should measure the desired constituent with precision and accuracy sufficient to meet the data needs of FWPCA, in the presence of the interferences normally encountered in polluted waters.

(2) The procedures should utilize the equipment and skills normally available in the typical water pollution control laboratory.

(3) The selected methods are in use in many laboratories or have been sufficiently tested to establish their validity.

(4) The methods should be sufficiently rapid to permit routine use for the examination of a large number of samples.

Except where noted under "Scope and Application" for each constituent, the methods are useful for the measurement of the indicated constituent in both water and wastewaters and in both saline and fresh water samples. Table I lists the parameter to be measured, the basis of the analytical method, the reference volume which contains a detailed description of the procedure, and the STORET number to be used in recording the final result. The reader should note that most of the detailed analytical procedures found in this manual will ultimately appear in Standard Methods for the Examination of Water and Wastewater, 13th Edition, and/or ASTM Standards, Part 23. A majority of the procedures have been

Preceding page blank

accepted for future publication and adoption by these organizations or are under consideration by the appropriate subcommittees.

The 1969 edition contains a number of procedures not included in previous publications of FWPCA methods. In particular, procedures are included for the use of the AutoAnalyzer for the determination of alkalinity, chloride, fluoride, hardness, Kjeldahl nitrogen, ammonia nitrogen, nitrate nitrogen, phosphorus, and sulfate. In certain cases two procedures are offered, since definitive data are not presently available to indicate a choice. Detailed instructions are also given for the measurement of metals by atomic absorption spectroscopy. The dissolved oxygen probe and the fluoride specific ion electrode are included as alternative methods.

Certain changes in recommended FWPCA methods have been made, notably (a) the use of the pyridine pyrazalone method for the determination of cyanide replacing the benzidine pyridine method; (b) the use of glass fiber filters instead of membrane filters in the determination of suspended solids; and (c) a drying temperature of 180°C in place of the previously recommended 105°C for dissolved solids measurement.

Specific instructions for the handling and preservation of samples cannot be given because of the wide variability in types of samples and local sampling situations. However, certain general principles should be followed. Wherever possible, the sampling program should be designed to provide for the shortest possible interval between sample collection and analysis. Positive steps should be taken to maintain both the concentration and the physical state of the constituents to be measured. Where both total and dissolved concentrations are to be determined, the dissolved concentration is the amount present after filtration through a 0.45 micron membrane filter. When the dissolved concentration is to be determined, filtration should be carried out as soon as possible after collection of the sample, preferably in the field. Where field filtration is not practical, the sample should be filtered as soon as it is received in the laboratory.

In situations where the interval between sample collection and analysis is long enough to produce significant changes in either the concentration or the physical state of the constituent to be measured, the preservatives listed in Table II are recommended.

Although every effort has been made to select methods which are applicable to the widest range of sample types, circumstances may require that alternative procedures be used in place of the methods recommended herein. In these situations, the analyst is urged to define the nature of the interference with the FWPCA method and bring this information to the attention of the Analytical Quality Control Laboratory through the appropriate Regional AQC Coordinator. The analyst should also suggest alternative procedures which have been found to be superior for this kind of sample condition. In this manner, any weaknesses in the selected methods and the preferable alternatives can be called to the attention of all laboratories utilizing the FWPCA methods.

The methods described herein were selected with the assistance of the following Regional Analytical Quality Control Coordinators:

Richard T. Dewling
AQC Coordinator
Hudson-Delaware Basins Office
Northeast Region, FWPCA
Edison, New Jersey 08817

Kenneth R. Tinsley
AQC Coordinator
Middle Atlantic Region, FWPCA
918 Emmet Street
Charlottesville, Virginia 22901

William T. Donaldson
AQC Coordinator
Southeast Water Laboratory
Southeast Region, FWPCA
College Station Road
Athens, Georgia 30601

Jacob D. Dumelle
ATTN: LeRoy E. Scarce
AQC Coordinator
Great Lakes Region, FWPCA
1819 West Pershing Road
Chicago, Illinois 60605

Theodore O. Meiggs
AQC Coordinator
Missouri Basin Region Laboratory
Missouri Basin Region, FWPCA
7300 Rochester Road, Box 4963
Kansas City, Missouri 64120

Robert E. Crowe
AQC Coordinator
Kerr Water Research Center
South Central Region, FWPCA
P. O. Box 1198
Ada, Oklahoma 74820

Daniel F. Krawczyk
AQC Coordinator
Pacific Northwest Water Laboratory
Northwest Region, FWPCA
200 South 35th Street
Corvallis, Oregon 97330

John C. Merrell, Jr.
AQC Coordinator
Southwest Region, FWPCA
Phelan Bldg., 760 Market Street
San Francisco, California 94102

Robert L. Booth
AQC Coordinator
Analytical Quality Control Laboratory
Ohio Basin Region, FWPCA
1014 Broadway
Cincinnati, Ohio 45202

FWPCA METHODS FOR CHEMICAL ANALYSIS

OF WATER AND WASTES

JULY, 1969

TABLE I

Parameter	Storet Number	Method	References to be Used		
			Std. Meth. 12th Ed. (1965)	ASTM Stds. Part 23 (1968)	USGS
Acidity, Total (mg/1 as $CaCO_3$)	00435	Electrometric titration - pH 8.3	This Manual		*
Alkalinity, Total (mg/1 as $CaCO_3$)	00410	Electrometric titration - pH 4.5 Technicon - Methyl Orange	 This Manual	p. 155	*
Aluminum, Total (µg/1 , Dissolved (µg/1)	-- 01105	Atomic Absorption Filtration through 0.45µ MF	This Manual		
Arsenic, Inorganic (µg/1)	01000	Silver diethyldithiocarbomate	p. 56-57		*
Biochemical Oxygen Demand, 5 day mg/1)	00310	Winkler-azide or DO analyzer	This Manual		
Cadmium, Total (µg/1) , Dissolved (µg/1)	-- 01025	Atomic Absorption Filtration through 0.45µ MF	This Manual		*
Calcium, Total (mg/1)	00915	Atomic Absorption	This Manual		*
Chemical Oxygen Demand (mg/1) Low Level (mg/1) Saline Waters (mg/1)	00340 00335 00340	Dichromate reflux - 0.25N - 0.025N - Chloride correction	p. 510-514 This Manual This Manual	p. 244	*

*(See USGS Reference, last page of index)

FWPCA METHODS FOR CHEMICAL ANALYSIS

OF WATER AND WASTES

Parameter	Storet Number	Method	References to be Used Std. Meth. 12th Ed. (1965)	ASTM Stds. Part 23 (1968)	USGS
Chloride (mg/l)	00940	Mercuric nitrate titration Technicon - Ferricyanide	p. 87-90 This Manual	p.24	*
Chlorine Demand, 15 min. (mg/l) 1 hr. (mg/l) 2 hr. (mg/l) 24 hr. (mg/l)	00365 00370 00375 00380	Amperometric titration	p. 381-383		
Chlorine Residual (mg/l)	50060	Amperometric titration	p. 378		
Chromium, Total (µg/l) , Dissolved (µg/l)	-- 01030	Atomic Absorption Filtration through 0.45µ MF	This Manual		*
Color, Units	00080	Platinum-cobalt visual	This Manual		*
Copper, Total (µg/l) , Dissolved (µg/l)	-- 01040	Atomic Absorption Filtration through 0.45µ MF	This Manual		*
Cyanide (mg/l)	00720	Silver nitrate titration or pyridine-pyrazalone	This Manual		*

*(See USGS Reference, last page of index)

FWPCA METHODS FOR CHEMICAL ANALYSIS

OF WATER AND WASTES

Parameter	Storet Number	Method	References to be Used Std. Meth. 12th Ed. (1965)	ASTM Stds. Part 23 (1968)	USGS
Dissolved Oxygen (mg/l)	00300	Winkler-azide or DO analyzer	This Manual		*
Fluoride (mg/l)	00950	SPADNS, with distillation Technicon - complexone Probe	p. 144-146 This Manual This Manual	p. 212-217	
Hardness, Total, (mg/l as $CaCO_3$)	00900	EDTA titration Technicon - E.B.T. Calculation - Ca + Mg by atomic absorption	p. 147-152 This Manual This Manual		*
Iron, Total (μg/l) , Dissolved (μg/l)	-- 01046	Atomic Absorption Filtration through 0.45μ MF	This Manual		*
Lead, Total (μg/l) , Dissolved (μg/l)	-- 01049	Atomic Absorption Filtration through 0.45μ MF	This Manual		*
Magnesium, Total (mg/l)	00925	Atomic Absorption	This Manual		*
Manganese, Total (μg/l) , Dissolved (μg/l)	-- 01055	Atomic Absorption Filtration t'rough 0.45 MF	This Manual		*

*(See USGS Reference, last page of index)

FWPCA METHODS FOR CHEMICAL ANALYSIS

OF WATER AND WASTES

Parameter	Storet Number	Method	References to be Used Std. Meth. 12th Ed. (1965)	ASTM Stds, Part 23 (1968)	USGS
MBAS (mg/l)	38260	Methylene Blue	p. 297-299		
Nitrogen, Ammonia (mg/l)	00610	Distillation (pH 9.5) - Nesslerization Technicon - sodium phenolate	This Manual This Manual		
Nitrogen, Kjeldahl, Total (mg/l)	00625	Digestion - distillation Technicon - digestion + phenolate	This Manual This Manual		
Nitrogen, Nitrate (mg/l)	00620	Brucine sulfate Technicon - hydrazine reduction	This Manual This Manual		*
Nitrogen, Nitrate - Nitrite (mg/l)		Technicon - cadmium reduction	This Manual		
Nitrogen, Nitrite (mg/l)	00615	Diazotization Technicon - diazotization	This Manual This Manual		*
Nitrogen, Organic + Ammonia (mg/l)	00635	Technicon - digestion + phenolate	This Manual		
Oil & Grease (mg/l)	00550	Hexane soxhlet extraction	This Manual		

*(See USGS Reference, last page of index)

FWPCA METHODS FOR CHEMICAL ANALYSIS

OF WATER AND WASTES

Parameter	Storet Number	Method	References to be Used Std. Meth. 12th Ed. (1965)	ASTM Stds. Part 23 (1968)	
Organic Carbon, Total (mg/l)	00680	Dow Beckman (MOD #915) or Carbonaceous Analyzer	This Manual		
, Dissolved (mg/l)	00681	Filtration through 0.45µ MF	This Manual		
pH (units)	00400	Electrometric	p. 226-228	p. 284	*
Phenolics (mg/l)	32730	4-aminoantipyrine	p. 516	p. 517	
Phosphorus, (mg/l)	00665	Persulfate - digestion + single reagent Technicon - manual digestion + automated single reagent or stannous chloride			
Hydrolyzable (mg/l)		Sulfuric acid digestion + single reagent Technicon - manual digestion + automated single reagent or stannous chloride	This Manual		*
Orthophosphate (mg/l)	70507	Direct single reagent Technicon - single reagent or stannous chloride			
Phosphorus, Dissolved	00666	Filtration through 0.45µ MF			
Potassium, Total (mg/l)	--	Atomic Absorption	This Manual		
, Dissolved (mg/l)	00935	Titration through 0.45µ MF			*

*(See USGS Reference, last page of index)

FWPCA METHODS FOR CHEMICAL ANALYSIS

OF WATER AND WASTES

Parameter	Storet Number	Method	References to be Used Std. Meth. 12th Ed. (1965)	 ASTM Stds. Part 23 (1968)	 USGS
Selenium, Total (g/l)	--	Diaminobenzidine	p.251-253		
, Dissolved (g/l)	01145	Filtration through 0.45μ MF			*
Silica, Total (μg/l)	--	Molybdate			
, Dissolved (μg/l)	00955	Filtration through 0.45μ MF			*
Sodium, Total (mg/l)	--	Atomic Absorption	This Manual		
, Dissolved (mg/l)	00930	Filtration through 0.45μ MF			*
Solids, Total (mg/l)	00500	Gravimetric, 105°C			
, filterable	00515	Filtration through glass fiber, 180°C	This Manual		
, non-filterable	00530	Glass-fiber filtration, 105°C			
, Volatile (mg/l)	00505	Gravimetric, 550°C	p. 425		
Specific Conductance	00095	Wheatstone Bridge	p. 280	p. 183	*
Sulfate (mg/l)	00945	Turbidimetric	p. 291-293	p. 56-58	
		Technicon - Barium chloranilate	This Manual		
Sulfide (mg/l)	00745	Iodometric	p. 428		*

*(See USGS Reference, last page of index)

FWPCA METHODS FOR CHEMICAL ANALYSIS

OF WATER AND WASTES

Parameter	Storet Number	Method	References to be Used		
			Std. Meth. 12th Ed. (1965)	ASTM Stds. Part 23 (1968)	USGS
Temperature (°C)	00010	Mercury, dial, or thermistor	p. 311		*
Threshold Odor - 60°C - Room Temp.	-- 00085	Dilution series Dilution series	p 304		
Turbidity, Nephelometric (JCU)	00070	Hach 2100 or equivalent	This Manual		*
Zinc, Total (ug/1) , Dissolved (ug/1)	-- 01090	Atomic Absorption Filtration through 0.45u MF	This Manual		*

*Techniques of Water Resources Investigations of the U.S. Geological Survey, Book 5, Chap AI: Laboratory Analysis of Water, Dissolved Minerals and Gases (to be published)

Table II - Sample Preservation

Parameter	Preservative	Maximum Holding Period
Acidity-Alkalinity	Refrigeration at 4°C	24 hours
Biochemical Oxygen Demand	Refrigeration at 4°C	6 hours
Calcium	None required	---
Chemical Oxygen Demand	2 ml H_2SO_4 per liter	7 days
Chloride	None required	---
Color	Refrigeration at 4°C	24 hours
Cyanide	NaOH to pH 10	24 hours
Dissolved Oxygen	Determine on site	No holding
Fluoride	None required	---
Hardness	None required	---
Metals, Total	5 ml HNO_3 per liter	6 months
Metals, Dissolved	Filtrate: 3 ml 1:1 HNO_3 per liter	6 months
Nitrogen, Ammonia	40 mg $HgCl_2$ per liter - 4°C	7 days
Nitrogen, Kjeldahl	40 mg $HgCl_2$ per liter - 4°C	Unstable
Nitrogen, Nitrate - Nitrite	40 mg $HgCl_2$ per liter - 4°C	7 days
Oil and Grease	2 ml H_2SO_4 per liter - 4°C	24 hours
Organic Carbon	2 ml H_2SO_4 per liter (pH 2)	7 days
pH	None available	---
Phenolics	1.0 g $CuSO_4$ + H_3PO_4 to pH 4.0 - 4°C	24 hours
Phosphorus	40 mg $HgCl_2$ per liter - 4°C	7 days

Table II - Sample Preservation
(continued)

Parameter	Preservative	Maximum Holding Period
Solids	None available	---
Specific Conductance	None required	---
Sulfate	Refrigeration at 4°C	7 days
Sulfide	2 ml Zn acetate per liter	7 days
Threshold Odor	Refrigeration at 4°C	24 hours
Turbidity	None available	---

References:

Jenkins, David, "A Study of Methods Suitable for the Analysis and Preservation of Phosphorus Forms in an Estuarine Environment." Report for the Central Pacific River Basins Project, Southwest Region, FWPCA (1965).

Jenkins, David, "A Study of Methods for the Analysis and Preservation of Nitrogen Forms in an Estuarine Environment." Report for Central Pacific River Basins Project, Southwest Region, FWPCA (1965).

Howe, L. H. and Holley, C. W. "Comparisons of Mercury (II) Chloride and Sulfunic Acid as Preservatives for Nitrogen Forms in Water Samples." Env. Sci. & Techn. 3:478 (1969).

ACIDITY

1. Scope and Application

1.1 The method recommended is identical to the procedure described in ASTM Standards, Part 23, pp 155-158, except that the sample is titrated to a final pH of 8.3 and results reported as mg/l $CaCO_3$.

1.2 This method is not applicable to analysis of acid samples from mine drainage. It is the decision of the AQC staff to delay the method selection for measurement of acidity in acid mine drainage samples until such time that a more comprehensive review of the problem can be made.

1.3 Methods for analysis of mine drainage samples for all constituents contributing to acidity of such samples may be selected at the option of the respective laboratory directors.

2. Calculation

2.1 Acidity is reported as calcium carbonate $CaCO_3$ according to the following formula:

$$\text{Acidity as mg/l } CaCO_3 = \frac{A \times N \times 50{,}000}{\text{ml sample}}$$

where:

A - ml of base used for titration

N = normality of base

3. Precision

3.1 A synthetic sample containing 21 mg/l acidity as $CaCO_3$ was analyzed by 55 laboratories with a standard deviation of ±1.73 mg/l.

Preceding page blank

TOTAL ALKALINITY

(Automated Methyl Orange Method)

1. Scope and Application

1.1 This automated method is applicable to surface and saline waters. The applicable range is 10 to 200 mg/1 as $CaCO_3$.

2. Summary of Method

2.1 Methyl orange is used as the indicator in this method because its pH range is in the same range as the equivalence point for total alkalinity, and it has a distinct color change that can be easily measured. The methyl orange is dissolved in a weak buffer at a pH of 3.1, just below the equivalence point, so that any addition of alkalinity causes a color change directly proportional to the amount of alkalinity.

3. Sample Handling and Preservation

3.1 Sample should be refrigerated at 4°C and run as soon as practical.

4. Interferences

4.1 No significant interferences.

5. Apparatus

5.1 Technicon AutoAnalyzer consisting of:

5.1.1 Sampler I.

5.1.2 Manifold.

5.1.3 Proportioning pump.

5.1.4 Colorimeter equipped with 15 mm tubular flow cell and 550 mμ filters.

5.1.5 Recorder equipped with range expander.

6. Reagents

6.1 Methyl Orange: Dissolve 0.125 g of methyl orange in 1 liter of distilled water.

6.2 pH 3.1 buffer: Dissolve 5.1047 g of potassium acid phthalate in distilled water and add 87.6 ml 0.1 N HCl and dilute to 1 liter. Stable for one week.

6.3 Methyl Orange-Buffered Indicator: Add 1.0 liter of pH 3.1 buffer to 200 ml methyl orange solution and mix well. Stable for 24 hours.

6.4 Stock Solution: Dissolve 1.0000 g of pre-dried anhydrous sodium carbonate in distilled water and dilute to 1.0 liter. 1.0 ml = 1.00 mg Na_2CO_3.

6.4.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 ml with distilled water. The following dilutions are suggested:

ml of Stock Solution	Conc. mg/l
1.0	10
2.0	20
4.0	40
6.0	60
8.0	80
10.0	100
14.0	140
18.0	180
20.0	200

7. Procedure

7.1 No advance sample preparation is required. Set up manifold as shown in Figure 1.

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.3 Place distilled water wash tubes in alternate openings on sampler and set sample timing at 2.0 minutes.

7.4 Place working standards in sampler in order of decreasing concentration. Complete filling of sampler tray with unknown samples.

7.5 Switch sample line from distilled water to sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (AQC), using surface water samples at concentrations of 15, 57, 154, and 193 mg/l as $CaCO_3$, the standard deviation was ±0.5.

9.2 In a single laboratory (AQC), using surface water samples at concentrations of 31 and 149 mg/l as $CaCO_3$, recoveries were 100% and 99%, respectively.

References

1. Technicon AutoAnalyzer Methodology, Bulletin 1261, Technicon Controls, Inc., Chauncey, N.Y. (1961).

2. Standard Methods, APHA, 12th Ed., p. 48, New York, N.Y. (1965).

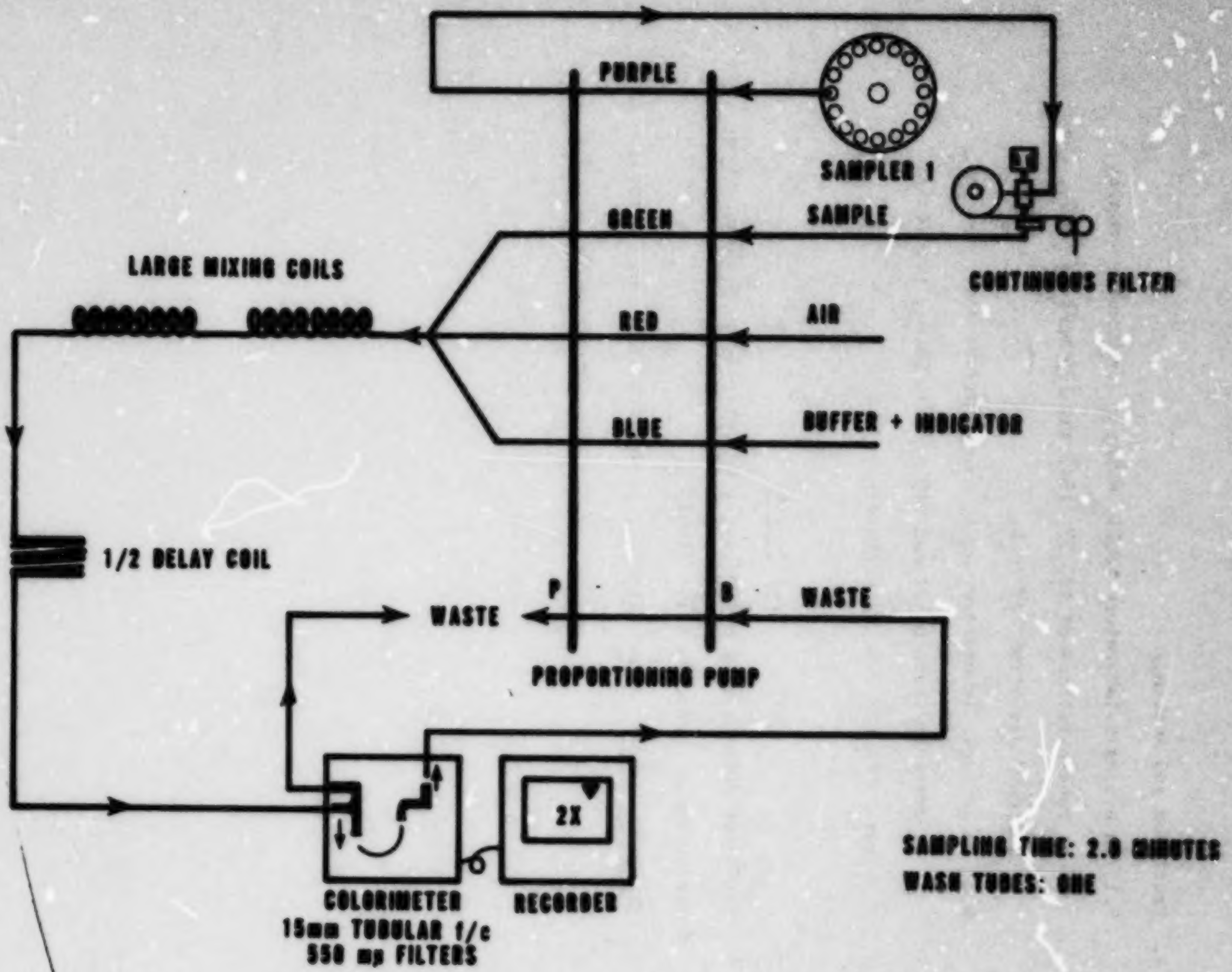

PURPLE
SAMPLER 1
GREEN
SAMPLE
CONTINUOUS FILTER
LARGE MIXING COILS
RED
AIR
BLUE
BUFFER + INDICATOR
1/2 DELAY COIL
P
B
WASTE
WASTE
PROPORTIONING PUMP
2X
COLORIMETER
15mm TUBULAR f/c
550 mμ FILTERS
RECORDER
SAMPLING TIME: 2.0 MINUTES
WASH TUBES: ONE

FIGURE 1. ALKALINITY MANIFOLD

BIOCHEMICAL OXYGEN DEMAND

1. Scope and Application

1.1 It is the opinion of the Analytical Quality Control Program and its advisors that present BOD test procedures are inherently nonreproducible and that the unpredictable nature of the test results make their interpretation difficult. Therefore, no specific procedure has been selected as the FWPCA standard test for Biochemical Oxygen Demand.

1.2 The traditional BOD test is empirical, employing standardized laboratory conditions in an attempt to yield reproducible results. Since the actual environmental conditions of temperature, biological population, water movement, sunlight, and oxygen concentrations cannot be accurately reproduced in the laboratory, the results obtained from the empirical test have little relationship to stream oxygen demands.

1.3 The test may be useful for determining the relative waste loadings to treatment plants and the degree of oxygen demand removal provided by primary treatment. Because of the complex changes in oxygen-demanding materials during secondary treatment, the use of the test to measure secondary plant efficiency is questionable.

1.4 At the present time, there are no other procedures that adequately replace the BOD test. There are, however, other measurements available which furnish useful information. These tests include Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD).

2. Procedure

2.1 Directions for conducting the BOD test are found in:

Standard Methods for the Examination of Water and Wastewater, 12 Edition (1965), pp. 415-421.

ASTM Standards (1968) Part 23, Water; Atmospheric Analyses, pp. 727-732.

2.2 Determinations of dissolved oxygen in the BOD test may be made by use of Dissolved Oxygen (Probe Method) or Dissolved Oxygen (Modified Winkler with Full-Bottle Technique) in this manual.

3. Precision and Accuracy

3.1 In 34 laboratories, the standard deviation of the BOD test, using a glucose-glutamic acid mixture, was ±31 mg/l at a mean BOD concentration of 184 mg/l. In a single laboratory, the precision was ±11 mg/l at a BOD of 218 mg/l (Analytical Reference Service, PHS).

3.2 There is no method available to determine the accuracy of the BOD test.

CHEMICAL OXYGEN DEMAND

(Low Level)

1. Scope and Application

   1.1 The scope of this modification of the Chemical Oxygen Demand (COD) test is the same as for the high level test. It is applicable to the analysis of surface waters, domestic and industrial wastes with low demand characteristics.

   1.2 This method (low level) is applicable for samples having a COD in the range of 5-50 mg/l COD.

2. Summary of Method

   2.1 Organic and oxidizable inorganic substances in an aqueous sample are oxidized by potassium dichromate solution in 50 percent (by volume) sulfuric acid solution. The excess dichromate is titrated with standard ferrous ammonium sulfate using orthophenanthroline ferrous complex (ferroin) as an indicator.

3. Sampling and Preservation

   3.1 Collect the samples in glass bottles, if possible. Use of plastic containers is permissible if it is known that no organic contaminants are present in the containers.

   3.2 Biologically active samples should be tested as soon as possible. Samples containing settleable material should be well mixed, preferably homogenized, to permit removal of representative aliquots.

3.3 Samples may be preserved with sulfuric acid at a rate of 2 ml of conc. H_2SO_4 per liter of sample.

4. Interferences

4.1 Traces of organic material either from the glassware or atmosphere may cause a gross, positive error.

4.1.1 Extreme care should be exercised to avoid inclusion of organic materials in the distilled water used for reagent preparation or sample dilution.

4.1.2 Glassware used in the test should be conditioned by running blank procedures to eliminate traces of organic material.

4.2 Volatile materials may be lost when the sample temperature rises during the sulfuric acid addition step.

4.3 Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion flask to complex the chlorides, thereby effectively eliminating the interference on all but brine samples.

5. Apparatus

5.1 Reflux apparatus - Glassware should consist of a 500 ml Erlenmeyer flask or a 300 ml round bottom flask made of heat-resistant glass connected to a 12 inch Allihn condenser by means of a ground glass joint. Any equivalent reflux apparatus may be substituted provided that a ground-glass connection is used between the flask and the condenser.

6. **Reagents**

6.1 Distilled water. Special precautions should be taken to insure that distilled water used in this test be low in organic matter.

6.2 Standard potassium dichromate solution (0.025 N) - Dissolve 12.259 g $K_2Cr_2O_7$, primary standard grade, previously dried at 103°C for two hours, in distilled water and dilute to 1000 ml. Mix this solution thoroughly then dilute 100 ml to one liter with distilled water.

6.3 Sulfuric acid reagent - Conc. H_2SO_4 containing 23.5 g silver sulfate, Ag_2SO_4, per 9 lb. bottle (one to two days required for dissolution).

6.4 Standard ferrous ammonium sulfate (0.025 N) - Dissolve 98 g of $Fe(NH_4)_2(SO_4)_2.6H_2O$ in distilled water. Add 20 ml of conc. H_2SO_4, cool and dilute to 1000 ml. Dilute 100 ml of this solution to one liter with distilled water. This solution must be standardized daily against $K_2Cr_2O_7$ solution.

6.4.1 Standardization - To 15 ml of distilled water add 10 ml of 0.025 N $Kr_2Cr_2O_7$ solution. Add 20 ml of H_2SO_4 and cool. Titrate with ferrous ammonium sulfate using 1 drop of ferroin indicator. The color change is sharp, going from blue-green to reddish-brown.

$$\text{Normality} = \frac{(\text{ml } K_2Cr_2O_7)\ (0.025)}{\text{ml Fe } (NH_4)_2(SO_4)_2}$$

6.5 Mercuric sulfate - Powdered $HgSO_4$.

6.6 Phenanthroline ferrous sulfate (ferroin) indicator solution - Dissolve 1.48 g of 1-10-(ortho)-phenanthroline monohydrate, together with 0.70 g of $FeSO_4.7H_2O$ in 100 ml of water. This indicator may be purchased already prepared.

6.7 Silver sulfate - Powdered Ag_2SO_4.

6.8 Sulfuric acid (sp. gr. 1.84) - Concentrated H_2SO_4.

7. Procedure

7.1 Place several boiling stones in the reflux flask, followed by 1 g of $HgSO_4$. Add 5.0 ml conc. H_2SO_4 (6.8); swirl until mercuric sulfate has dissolved. Place reflux flask in an ice bath and slowly add, with swirling, 25.0 ml of 0.025 N $K_2Cr_2O_7$. Now add 70.0 ml of sulfuric acid-silver sulfate solution (6.3) to the cooled reflux flask, again using slow addition with swirling motion.

7.2 With the reflux flask still in the ice bath, place 50.0 ml of sample or a sample aliquot diluted to 50.0 ml into the reflux flask. Caution: Care must be taken to assure that the contents of the flask are well mixed. If not, superheating may result, and the mixture may be blown out of the open end of the condenser. Attach the flask to the condenser and start the cooling water.

7.3 Apply heat to the flask and reflux for 2 hours. For some waste waters, the 2-hour reflux period is not necessary. The time required to give the maximum oxidation for a waste water of constant or known composition may be determined and a shorter period of refluxing may be permissible.

7.4 Allow the flask to cool and wash down the condenser with about 25 ml of water. If a round bottom flask has been used, transfer the mixture to a 500-ml Erlenmeyer flask, washing out the reflux flask 3 or 4 times with water. Dilute the acid solution to about 300 ml with water and allow the solution to cool to about room temperature. Add 8 to 10 drops of phenanthroline ferrous sulfate solution to the solution and titrate the excess dichromate with 0.025 N ferrous ammonium sulfate solution to the end point. The color change will be sharp, changing from a blue-green to a reddish hue.

7.5 Blank - Simultaneously run a blank determination following the details given in 7.1 and 7.2, but using low COD water in place of the sample.

8. Calculation

8.1 Calculate the COD in the sample in mg/l as follows:

$$\text{COD, mg/liter} = \frac{(A - B)\ N \times 8000}{S}$$

where:

A = milliliters of Fe $(NH_4)_2(SO_4)_2$ solution required for titration of the blank,

B = milliliters of $Fe(NH_4)_2(SO_4)_2$ solution required for titration of the sample,

N = normality of the Fe $(NH_4)_2(SO_4)_2$ solution, and

S = milliliters of sample used for the test.

9. Precision

9.1 The precision of the low level test described in the foregoing material has not been determined by collaborative testing.

CHEMICAL OXYGEN DEMAND

(High Level for Saline Waters)

1. Scope and Application

1.1 When the chloride level exceeds 1000 mg/l the minimum accepted value for the COD will be 250 mg/l. COD levels which fall below this value are highly questionable because of the high chloride correction which must be made.

2. Summary of Method

2.1 Organic and oxidizable inorganic substances in an aqueous sample are oxidized by potassium dichromate solution in 50 percent (by volume) sulfuric acid solution. The excess dichromate is titrated with standard ferrous ammonium sulfate using orthophenanthroline ferrous complex (ferroin) as an indicator.

3. Sample Handling and Preservation

3.1 Collect the samples in glass bottles, if possible. Use of plastic containers is permissible if it is known that no organic contaminants are present in the containers.

3.2 Biologically active samples should be tested as soon as possible. Samples containing settleable material should be well mixed, preferably homogenized, to permit removal of representative aliquots.

3.3 Samples are preserved by the addition of 2 ml of conc. H_2SO_4 per liter of sample.

4. Interferences

4.1 Traces of organic material either from the glassware or atmosphere may cause a gross, positive error.

4.1.1 Extreme care should be exercised to avoid inclusion of organic materials in the distilled water used for reagent preparation or sample dilution.

4.1.2 Glassware used in the test should be conditioned by running blank procedures to eliminate traces of organic material.

4.2 Volatile materials may be lost when the sample temperature rises during the sulfuric acid addition step.

4.3 Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion flask to complex the chlorides, thereby effectively eliminating the interference on all but brine samples.

5. Apparatus

5.1 Reflux apparatus - Glassware should consist of a 500 ml Erlenmeyer flask or a 300 ml round bottom flask made of heat-resistant glass connected to a 12 inch Allihn condenser by means of a ground glass joint. Any equivalent reflux apparatus may be substituted provided that a ground-glass connection is used between the flask and the condenser.

6. Reagents

6.1 Standard potassium dichromate solution, (0.25 N): Dissolve 12.2588 g of $K_2Cr_2O_7$, primary standard grade, previously dried for 2 hours at 103°C in water and dilute to 1.0 liter.

6.2 Sulfuric acid reagent: Conc. H_2SO_4 containing 23.5 g silver sulfate, Ag_2SO_4, per 9 lb. bottle (1 to 2 days required for dissolution).

6.3 Standard ferrous ammonium sulfate, 0.250 N: Dissolve 98 g of $Fe(NH_4)_2(SO_4)_2.6H_2O$ in distilled water. Add 20 ml of conc. H_2SO_4, cool and dilute to 1000 ml. This solution must be standardized against the standard potassium dichromate solution daily.

6.3.1 Standardization: Dilute 25.0 ml of standard dichromate solution to about 250 ml with distilled water. Add 75 ml conc. sulfuric acid. Cool, then titrate with ferrous ammonium sulfate titrant, using 10 drops of ferroin indicator.

$$\text{Normality} = \frac{(\text{ml } K_2Cr_2O_7)\ (0.25)}{\text{ml } Fe(NH_4)_2(SO_4)_2}$$

6.4 Mercuric sulfate - Powdered $HgSO_4$.

6.5 Phenanthroline ferrous sulfate (ferroin) indicator solution - Dissolve 1.48 g of 1-10-(ortho)-phenanthroline monohydrate, together with 0.70 g of $FeSO_4.7H_2O$ in 100 ml of water. This indicator may be purchased already prepared.

6.6 Silver sulfate - Powdered Ag_2SO_4.

6.7 Sulfuric acid (sp. gr. 1.84) - Concentrated H_2SO_4.

7. Procedure

7.1 Pipet a 50 ml aliquot of sample not to exceed 800 mg/l of COD into a 500 ml, flat bottom, Erlenmeyer flask. Add 25 ml of 0.25 N $Kr_2Cr_2O_7$, then 5.0 ml of conc. H_2SO_4 (containing no silver sulfate). Add $HgSO_4$ in the ratio of 10 mg to 1 mg chloride, based upon the mg of chloride in the sample aliquot. Swirl until all the mercuric sulfate has dissolved. Carefully add 70 ml of sulfuric acid-silver sulfate solution and gently swirl until the solution is thoroughly mixed. Glass beads should be added to the reflux mixture to prevent bumping, which can be severe and dangerous. (CAUTION: The reflux mixture must be thoroughly mixed before heat is applied. If this is not done, local heating occurs in the bottom of the flask, and the mixture may be blown out of the condenser).

7.1.1 If volatile organics are present in the sample, use an Allihn condenser and add the sulfuric acid-silver sulfate solution through the condenser, while cooling the flask, to reduce loss by volatilization.

7.2 Attach the flask to the condenser and reflux the mixture for two hours.

7.3 Cool, and wash down the interior of the condenser with 25 ml of distilled water. Disconnect the condenser and wash the flask and condenser joint with 25 ml of distilled water. Remove the condenser and carefully add to the flask 175 ml of distilled water so that the total volume is 350 ml. Cool to room temperature.

7.4 Titrate with standard ferrous ammonium sulfate using 10 drops of ferroin indicator. (This amount must not vary from blank, sample and standardization). The color change is sharp, going from blue-green to reddish-brown and should be taken as the end point although the blue-green color may reappear within minutes.

7.5 Run a blank, using 50 ml of distilled water in place of the sample together with all reagents and subsequent treatment.

7.6 For COD values greater than 800 ml, a smaller aliquot of sample should be taken; however, the volume should be readjusted to 50 ml with distilled water having a chloride concentration equal to the sample.

7.7 Chloride correction* - Prepare a standard curve of COD versus mg/l of chloride, using sodium chloride solutions of varying concentrations following exactly the procedure outlined. The chloride interval, as a minimum should be 4000 mg/l up to 20,000 mg/l chloride. Lesser intervals of greater concentrations must be run as per the requirements of the data, but in no case must extrapolation be used.

---

*Burns, E. R., Craig, N., Journal WPCF, Vol. 37, pp 1716-1721, 1967.

8. Calculation

8.1

$$\text{mg/l COD} = \frac{(A - B)\, C \times 8000}{\text{ml sample}} - D \times 1.20$$

where:

COD = chemical oxygen demand from dichromate

A = ml $Fe(NH_4)_2(SO_4)_2$ for blank;

B = ml $Fe(NH_4)_2(SO_4)_2$ for sample;

C = normality of $Fe(NH_4)_2(SO_4)_2$;

D = chloride correction from curve (step 7.7).

1.20 = compensation factor to account for the extent of chloride oxidation which is dissimilar in systems containing organic and nonorganic material.

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

CHLORIDE

(Automated Ferricyanide Method)

1. Scope and Application

1.1 This automated method is applicable on surface water, domestic and industrial wastes, and saline waters. The applicable range is 1 to 250 mg Cl/l. Approximately 15 samples per hour can be analyzed.

2. Summary of Method

2.1 Thiocyanate ion (SCN) is liberated from mercuric thiocyanate, through sequestration of mercury by chloride ion to form un-ionized mercuric chloride. In the presence of ferric ion, the liberated SCN forms highly colored ferric thiocyanate, in concentration proportional to the original chloride concentration.

3. Sample Handling and Preservation

3.1 No special requirements.

4. Interferences

4.1 No significant interferences.

5. Apparatus

5.1 Technicon AutoAnalyzer consisting of:

5.1.1 Sampler I.

5.1.2 Continuous filter.

5.1.3 Manifold.

5.1.4 Proportioning pump.

5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 400 mμ filters.

5.1.6 Recorder

6. Reagents

6.1 Ferric Ammonium Sulfate: Dissolve 60 g of $FeNH_4(SO_4)_2 \cdot 12H_2O$ in approximately 500 ml distilled water. Add 355 ml of conc HNO_3 and dilute to 1 liter with distilled water. Filter.

6.2 Saturated Mercuric Thiocyanate: Dissolve 5 g of $Hg(SCN)_2$ in 1 liter of distilled water. Decant and filter a portion of the saturated supernatant liquid to use as the reagent and refill the bottle with distilled water.

6.3 Stock Solution (0.141 N NaCl): Dissolve 0.8241 g of pre-dried NaCl in distilled water. Dilute to 1 liter. 1 ml = 0.5 mg Cl^-.

6.3.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 ml with distilled water. The following dilutions are suggested:

ml of Stock Solution	Conc., mg/l
0.2	1.0
1.0	5.0
2.0	10
4.0	20
8.0	40
15.0	75
20.0	100
30.0	150
40.0	200
50.0	250

7. Procedure

7.1 No advance sample preparation is required. Set up manifold as shown in Figure 1. For water samples known to be consistently low in chloride content, it is advisable to use only one distilled water intake line.

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.3 Place distilled water wash tubes in alternate openings in sampler and set sample timing at 2.0 minutes.

7.4 Place working standards in sampler in order of decreasing concentrations. Complete filling of sampler tray with unknown samples.

7.5 Switch sample line from distilled water to sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

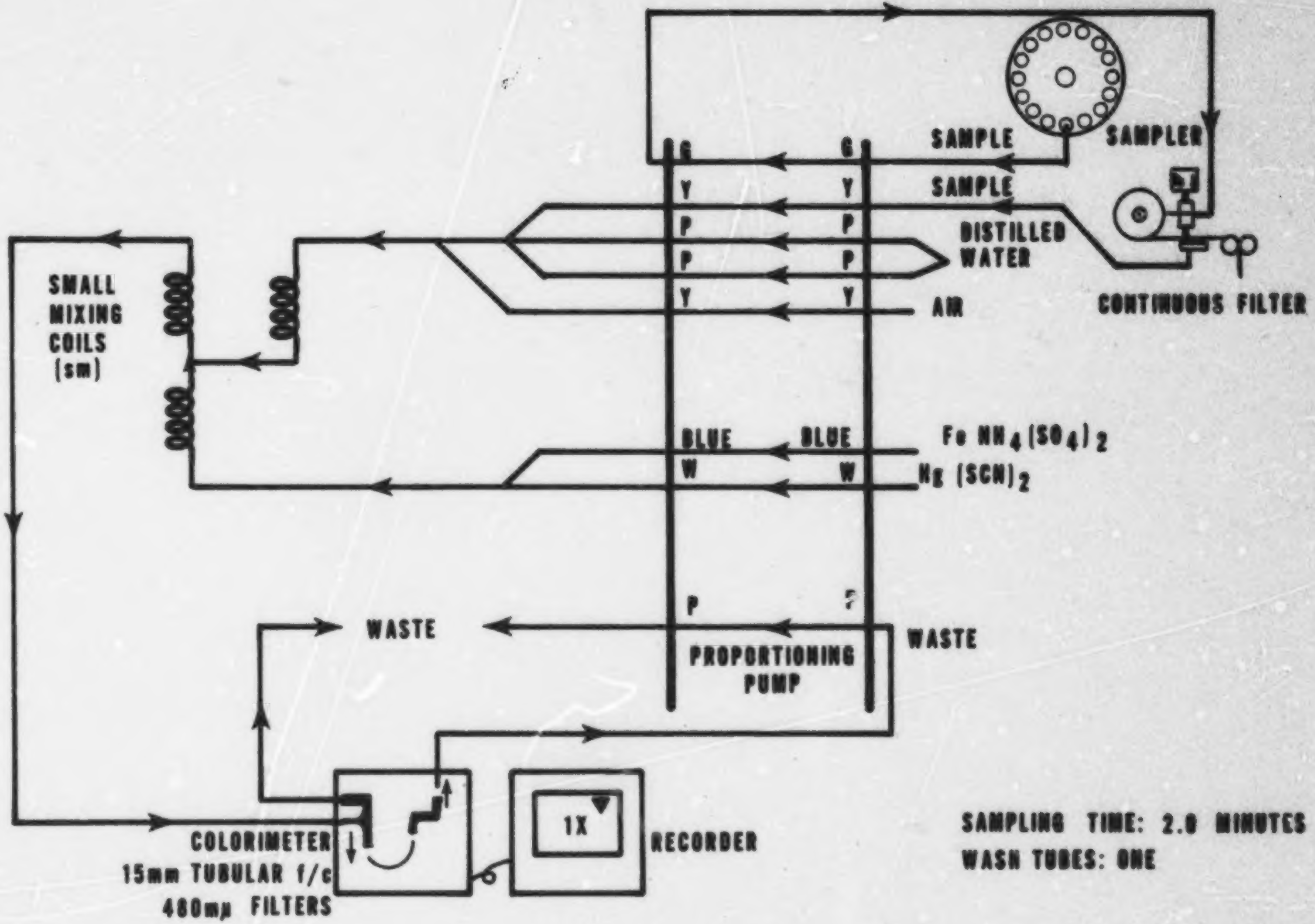
9. Precision and Accuracy

9.1 In a single laboratory, using surface water samples at concentrations of 1, 100, and 250 mg Cl^-/l, the standard deviation was ±0.3 (AQC Laboratory).

9.2 In a single laboratory (AQC), using surface water samples at concentrations of 10 and 100 mg Cl/l. recoveries were 97% and 104%, respectively.

Reference

1. J. E. O'Brien, "Automatic Analysis of Chlorides in Sewage," Wastes Engr., 33, 670-672 (Dec. 1962).


SAMPLER
SAMPLE
SAMPLE
DISTILLED WATER
AIR
CONTINUOUS FILTER
G
Y
P
P
Y
BLUE
W
P
G
Y
P
P
Y
BLUE
W
P
Fe NH$_4$(SO$_4$)$_2$
Hg (SCN)$_2$
SMALL MIXING COILS (sm)
WASTE
WASTE
PROPORTIONING PUMP
COLORIMETER
15mm TUBULAR f/c
480mμ FILTERS
1X
RECORDER

SAMPLING TIME: 2.0 MINUTES
WASH TUBES: ONE

FIGURE 1. CHLORIDE MANIFOLD

COLOR

1. Scope and Application

1.1 The Platinum-Cobalt method is useful for measuring color of water derived from naturally occurring materials, i.e., vegetable residues such as leaves, barks, roots, humus and peat materials. The method is not applicable to color measurement on waters containing highly colored industrial wastes.

Note - The Spectrophotometric and Tristimulus methods are useful for detecting specific color problems. The use of these methods, however, is laborious and unless determination of the hue, purity, and luminance is desired, they are of limited value.

2. Summary of Method

2.1 Color is measured by visual comparison of the sample with platinum-cobalt standards. One unit of color is that produced by 1 mg/l platinum in the form of the chloroplatinate ion.

3. Interference

3.1 Since very slight amounts of turbidity interfere with the determination, samples showing visible turbidity should be clarified by centrifugation.

Preceding page blank

4. Sample Handling and Preservation

4.1 Representative samples shall be taken in scrupulously clean glassware.

4.2 Since biological activity may change the color characteristics of a sample, the determination should be made as soon as possible. Refrigeration at 4°C is recommended.

5. Apparatus

5.1 Nessler tubes - Matched, tall form, 50 ml capacity.

6. Reagents

6.1 Standard chloroplatinate solution. Dissolve 1.246 g potassium chloroplatinate, K_2PtCl_6, (equivalent to 0.500 g metallic Pt) and 1 g crystalline cobaltous chloride, $CoCl_2.6H_2O$, in distilled water containing 100 ml of conc. HCl. Dilute to 1 liter with distilled water. This standard solution is equivalent to 500 color units.

7. Preparation of Standards

7.1 Prepare standards in increments from 5 to 70 units.

The following series is suggested:

ml of Standard Solution Diluted to 50.0 ml with Distilled Water	Color in Chloroplatinate Units
0.0	0
0.5	5
1.0	10
1.5	15
2.0	20
2.5	25
3.0	30
3.5	35
4.0	40
4.5	45
5.0	50
6.0	60
7.0	70

7.2 Protect these standards against evaporation and contamination by use of clean, inert stoppers.

Note - The standards also must be protected against the absorption of ammonia since an increase in color will result.

8. Procedure

8.1 Apparent color - Observe the color of the sample by filling a matched Nessler tube to the 50 ml mark with the water and compare with standards. This comparison is made by looking vertically downward through the tubes toward a white or specular surface placed at such an angle that light is reflected upward through the columns of liquid. If turbidity has not been removed by the procedure given in 8.2, report the color as "apparent color." If the color exceeds 70 units, dilute the sample with distilled water in known proportions until the color is within the range of the standards.

8.2 True color - Remove turbidity by centrifuging the sample until the supernatant is clear. Compare the centrifuged sample with distilled water to insure that turbidity has been removed. If the sample is clear, then compare with standards as given in 8.1.

9. Calculation

9.1 Calculate the color units by means of the following equation:

$$\text{Color units} = \frac{A \times 50}{V}$$

Where: A = estimated color of diluted sample.

V = ml sample taken for dilution.

9.2 Report the results in whole numbers as follows:

Color Units	Record to Nearest
1-50	1
51-100	5
101-250	10
251-500	20

10. Precision and Accuracy

10.1 Precision and accuracy data are not available at this time.

Reference - Standard Methods for the Examination of Water and Wastewater, 12th Edition, 127-129, 1965. APHA Inc., N.Y.

CYANIDE

1. Scope and Application

1.1 This method is applicable to the determination of cyanide in surface waters, domestic and industrial wastes, and saline waters.

1.2 The titration procedure using silver nitrate with p-dimethylamino-benzalrhodanine indicator is used for measuring concentrations of cyanide exceeding 1 mg/l (0.2 mg/200 ml of absorbing liquid).

1.3 The colorimetric procedure is used for concentrations below 1 mg/l of cyanide and is sensitive to about 5 μg/l.

2. Summary of Method

2.1 The cyanide as hydrocyanic acid (HCN) is released from metallic cyanide complex ions by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.

2.2 The colorimetric measurement employs the pyridine-pyrazolone reaction in which the cyanide is coupled with free chlorine to form cyanogen chloride and then with pyridine to a glutaconic aldehyde. The aldehyde then reacts with 1-phenyl-3-methyl-5-pyrazolone to form a highly colored blue dye.

2.3 The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3. Definitions

3.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium and mercuric ions.

4. Sample Handling and Preservation

4.1 The sample should be collected in plastic bottles of 1 liter or larger size. All bottles must be thoroughly cleansed and thoroughly rinsed to remove soluble material from containers.

4.2 Samples must be preserved with 20 ml of a 1 N sodium hydroxide per liter of sample at the time of collection.

4.3 Samples should be analyzed as rapidly as possible after collection. If storage is required, the samples should be stored in a refrigerator or in an ice chest filled with water and ice to maintain temperatures at 4°C.

5. Interferences

5.1 Interferences are eliminated or reduced by using the distillate obtained with the preliminary screening procedure.

5.2 Sulfides are an interference that should be removed prior to distillation. Remove sulfides with pH adjustment to >11, addition of lead carbonate and mixing. Filter sample to remove lead sulfide. Repeat until no more lead sulfide is formed as evidenced by whiteness of the lead carbonate.

5.3 Oxidizing substances interfere and should be treated with ascorbic acid.

6. Apparatus

6.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of 1 liter size with inlet tube and provision for condenser.

6.2 Microburet, 5.0 ml (for titration).

6.3 Spectrophotometer suitable for measurements at 620 mμ with a 1.0 cm cell or larger.

7. Reagents

7.1 Sodium hydroxide solution, 1 N. Dissolve 40 g of NaOH in distilled water, and dilute to a liter with distilled water.

7.2 Lead carbonate.

7.3 Ascorbic acid.

7.4 Mercuric chloride solution. Dissolve 34 g $HgCl_2$ in 500 ml distilled water.

7.5 Magnesium chloride solution. Dissolve 51 g $MgCl_2.6H_2O$ in 100 ml distilled water.

7.6 Sulfuric acid, concentrated.

7.7 Sodium dihydrogenphosphate, 1 M. Dissolve 138 g of $NaH_2PO_4.H_2O$ in a liter of distilled water. Refrigerate this solution.

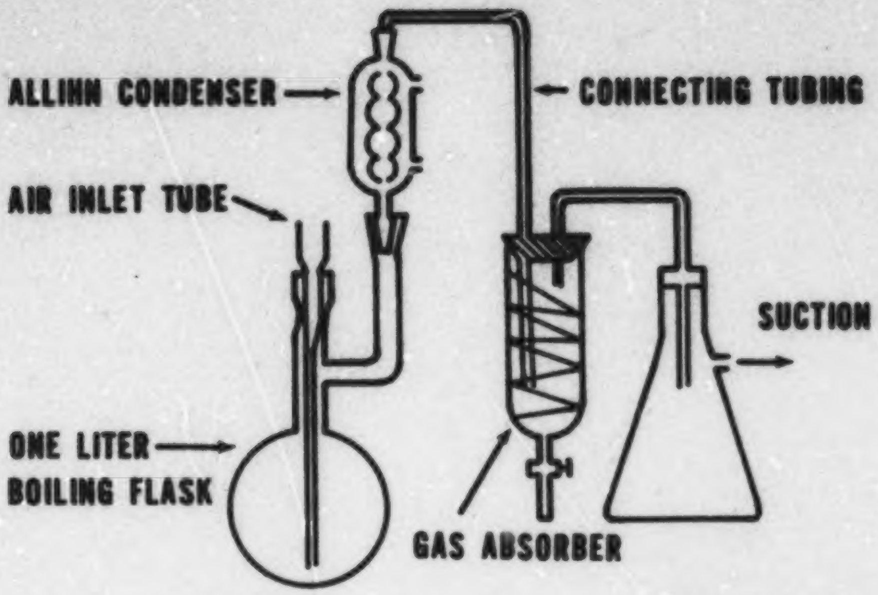

ALLIHN CONDENSER
CONNECTING TUBING
AIR INLET TUBE
SUCTION
ONE LITER BOILING FLASK
GAS ABSORBER

FIGURE 1

CYANIDE DISTILLATION APPARATUS

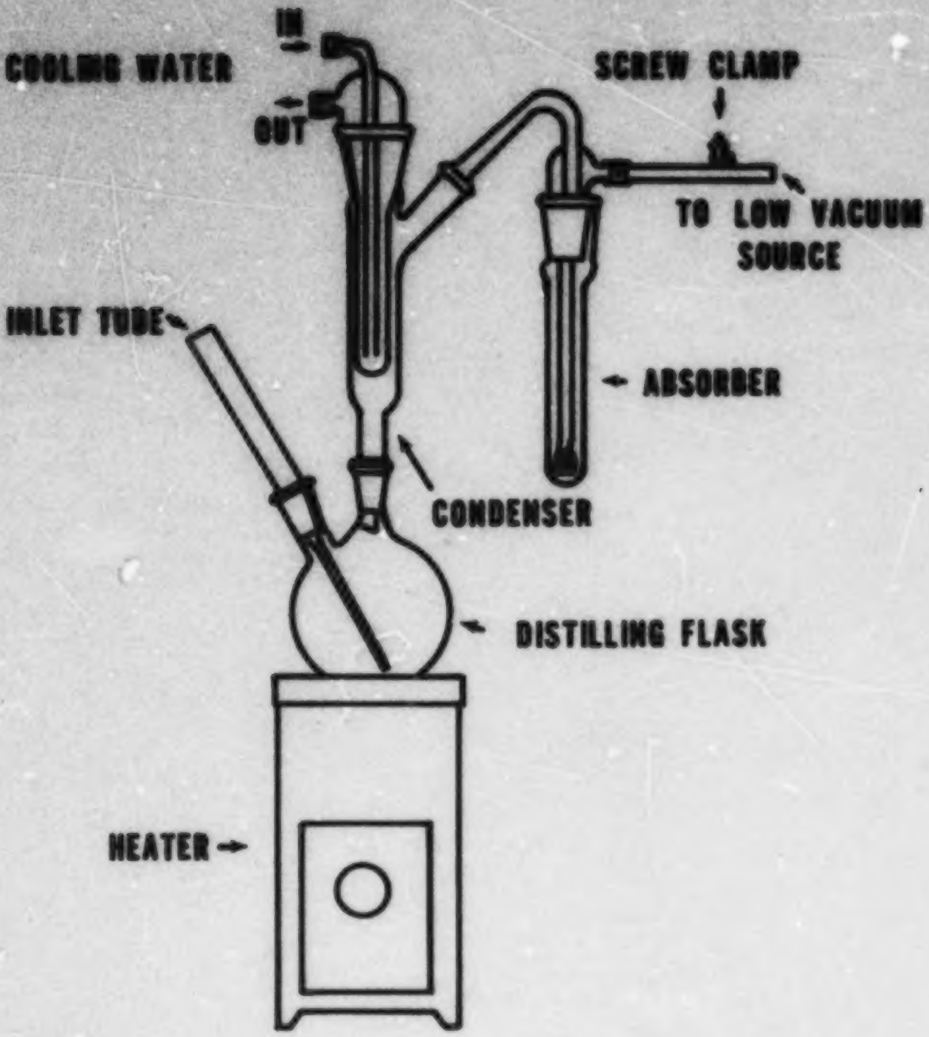

IN
COOLING WATER
OUT
SCREW CLAMP
TO LOW VACUUM SOURCE
INLET TUBE
ABSORBER
CONDENSER
DISTILLING FLASK
HEATER

FIGURE 2

CYANIDE DISTILLATION APPARATUS

7.8 Stock cyanide solution. Dissolve 2.51 g of KCN and 2 g KOH in a liter of distilled water. Standardize with 0.0192 N $AgNO_3$. Dilute to appropriate concentration so that 1 ml = 1 mg CN^-.

7.9 Standard cyanide solution, intermediate. Dilute 10 ml of stock (1 ml = 1 mg CN) to a liter of distilled water (1 ml = 10 μg).

7.10 Standard cyanide solution. Prepare fresh daily by diluting 100 ml of intermediate cyanide solution to a liter of distilled water and store in a glass stoppered bottle. One ml = 1.0 μg CN (1.0 ppm).

7.11 Standard silver nitrate solution, 0.0192 N. Prepare by crushing approximately 5 g $AgNO_3$ crystals and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgNO_3$, dissolve in water, and dilute to liter (1 ml = 1 mg CN).

7.12 Rhodanine indicator. Dissolve 20 mg of p-dimethylaminobenzalrhodanine in 100 ml of acetone.

7.13 Chloramine T solution. Dissolve 1.0 g of white water soluble Chloramine T in 100 ml of distilled water and refrigerate until ready to use. Prepare fresh weekly.

7.14 Pyridine-pyrazolone solution.

7.14.1 One-phenyl-3-methyl-5-pyrazolone reagent. Weigh 0.25 g of 3-methyl-1-phenyl-2-pyrazolone-5-one and

Preceding page blank

dissolve in 50 ml of distilled water by heating to 60°C. Cool after reagent is in solution.

7.14.2 Three,3'-Dimethyl-1,1'-diphenyl-4,4'-bi-2 pyrazolone - 5,5' dione (bispyrazolone). Dissolve 0.01 g of bispyrazolone in 10 ml of pyridine.

7.14.3 Pour solution 7.14.1 through nonacid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution 7.14.2 collecting the filtrate in the same container as filtrate from 7.14.1. Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.

8. Procedure

8.1 Place 500 ml of sample, or an aliquot diluted to 500 ml in the 1-liter boiling flask. Add 50 ml of 1 N sodium hydroxide (7.1) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber and trap in the train.

8.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately 1 bubble of air per second enters the boiling flask through the air inlet tube. (Caution: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.)

8.3 Add 10 ml of mercuric chloride solution (7.4) and 40 ml of magnesium chloride solution (7.5) through the air inlet tube. Rinse the air inlet tube with a few ml of distilled water and allow the air flow to mix the contents of the flask for at least 3 minutes.

8.4 Slowly add 25 ml of concentrated sulfuric acid (7.6) through the air inlet tube and rinse with distilled water.

8.5 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling of the boiling flask disconnect absorber and close off the vacuum source.

8.6 Drain the solution from the absorber into a 250 ml volumetric flask and bring up to volume with distilled water washings from the absorber tube. Cool the volumetric flask in an ice bath until the temperature of the solution is 5°C.

8.7 Withdraw 50 ml of the solution from the volumetric flask and transfer to a 100-ml volumetric flask. Add 10 ml of sodium phosphate solution (7.7) and 0.2 ml of Chloramine T solution (7.13) and mix. Add an additional 5 ml of the sodium phosphate (7.7), followed by 5 ml of mixed pyridine-pyrazolone solution, (7.14.3), bring to mark with distilled water and mix. Allow 40 minutes for color development.

8.8 Read absorbance at 620 mµ using at least a 1.0 cm cell.

8.9 Prepare a series of standards by diluting suitable volumes of standard solution to 500.0 ml with distilled water as follows:

ml of Standard Solution (1.0 ml = 1 µg CN)	Conc., When Diluted to 500 ml, mg/l CN
0 (Blank)	0
5.0	0.01
10.0	0.02
20.0	0.04
50.0	0.10
100.0	0.20
150.0	0.30
200.0	0.40

8.9.1 Standards must be treated in the same manner as the samples, as outlined in 8.1 through 8.8 above.

8.9.2 Prepare a standard curve by plotting absorbance of standards vs. cyanide concentrations.

8.9.3 Subsequently, at least two standards (a high and a low) should be treated as in 8.9.1 to verify standard curve. If results are not comparable (±20%), a complete new standard curve must be prepared.

8.9.4 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (7.9) or the working standard (7.10) to insure a level of 10 μg/l or a significant increase in absorbance value. Proceed with the analysis as in Procedure (8.) using the same flask and system from which the previous sample was just distilled.

8.10 Alternatively, if the sample contains more than 1 mg of CN^- transfer the distillate, or a suitable aliquot diluted to 250 ml, to a 500-ml Erlenmeyer flask. Add 10-12 drops of the benzalrhodanine indicator.

8.11 Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as the sample.

8.12 The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5 or 10 ml microburet may be conveniently used to obtain a more precise titration.

9. Calculation

9.1 Using the colorimetric procedure, calculate concentration of CN, mg/l, directly from prepared standard curve.

9.2 Using the titrimetric procedure, calculate concentration of CN as follows:

$$\text{CN, mg/l} = \frac{(A-B) \times 1000}{\text{Vol. of original sample}} \times \frac{250}{\text{Vol. of aliquot titrated}}$$

where:

A = volume of $AgNO_3$ for titration of sample.

B = volume of $AgNO_3$ for titration of blank.

10. Precision and Accuracy

10.1 A synthetic sample prepared by the Analytical Reference Service (PHS) at a known concentration of 0.02 mg/l CN was analyzed by 47 analysts; the data showed a standard deviation of 0.035 mg/l for the titrimetric procedure and 0.020 mg/l for the colorimetric procedure. Similarly, at a concentration of 1.10 mg/l of CN, the data showed a standard deviation of 0.333 mg/l for the titrimetric procedure and 0.306 mg/l for the colorimetric procedure.

References

1. Bark, L. S., and Higson, H. G. Investigation of reagents for the colorimetric determination of small amounts of cyanide. Talanta, 2:471-479 (1964).
2. Ely, C. T. Recovery of cyanides by modified Serfass distillation. Journal Water Pollution Control Federation, 40:848-856 (1968).

DISSOLVED OXYGEN

(Modified Winkler With Full-Bottle Technique)

1. Scope and Application

1.1 This method is applicable for use with most wastewaters and streams that contain nitrite nitrogen and not more than 1 mg/l of ferrous iron. Other reducing or oxidizing materials should be absent. If 1 ml fluoride solution is added before acidifying the sample and there is no delay in titration, the method is also applicable in the presence of 100-200 mg/l ferric iron.

1.2 The azide modification is not applicable under the following conditions: (a) samples containing sulfite, thiosulfate, polythionate, appreciable quantities of free chlorine or hypochlorite; (b) samples high in suspended solids; (c) samples containing organic substances which are readily oxidized in a highly alkaline solution, or which are oxidized by free iodine in an acid solution; (d) domestic sewage; (3) biological flocs; and (f) where sample color interferes with endpoint detection. In instances where the azide modification is not applicable, a DO probe should be used.

2. Summary of Method

2.1 The sample is treated with manganous sulfate, potassium hydroxide, and potassium iodide (the latter two reagents combined in one solution) and finally sulfuric acid. The initial precipitate of manganous hydroxide, $Mn(OH)_2$, combines with the dissolved oxygen in the sample to form a brown precipitate, manganic hydroxide, $Mn\,O(OH)_2$. Upon acidification, the manganic hydroxide forms manganic sulfate which acts as an oxidizing agent to release free iodine from the potassium iodide. The iodine, which is stoichiometrically equivalent to the dissolved oxygen in the sample is then titrated with sodium thiosulfate.

3. Interferences

3.1 There are a number of interferences to the dissolved oxygen test, including oxidizing and reducing agents, nitrite ion, ferrous iron, and organic matter.

3.2 Various modifications of the original Winkler procedure for dissolved oxygen have been developed to compensate or eliminate interferences. The Alsterberg modification is commonly used to successfully eliminate the nitrite interference, the Rideal-Stewart modification is designed to eliminate ferrous iron interference, and the Theriault procedure is used to compensate for high concentration of organic materials.

3.3 Most of the common interferences in the Winkler procedure may be overcome by use of the dissolved oxygen probe.

4. Sample Handling and Preservation

4.1 Where possible, collect the sample in a 300 ml BOD incubation bottle. Special precautions are required to avoid entrainment or solution of atmospheric oxygen or dissolution of dissolved oxygen.

4.2 Where samples are collected from shallow depths (less than 5 feet), use of an APHA-type sampler is recommended. Use of a Kemmerer type sampler is recommended for samples collected from depths of greater than 5 feet.

4.3 When a Kemmerer sampler is used, the BOD sample bottle should be filled to overflowing. (Overflow for approximately 10 seconds.) Outlet tube of Kemmerer should be inserted to bottom of BOD bottle. Care must be taken to prevent turbulence and the formation of bubbles when filling bottle.

4.4 The sample temperature should be recorded at time of sampling as precisely as required.

4.5 Do not delay the determination of dissolved oxygen in samples having an appreciable iodine demand or containing ferrous iron. If samples must be preserved either method 4.5.1 or 4.5.2, below, may be employed.

4.5.1 Add 2 ml of manganous sulfate reagent and then 2 ml of alkali azide reagent to the sample contained in the BOD bottle. Both reagents must be added well below the surface of the liquid. Stopper the bottle immediately and mix the contents thoroughly. The sample should be stored at the temperature of the collection water, or water sealed and kept at a temperature of 10 to 20°C, in the dark.

entrainment or solution of atmospheric oxygen or dissolution of dissolved oxygen.

4.2 Where samples are collected from shallow depths (less than five feet) use of an APHA-type sampler is recommended. Use of a Kemmerer type sampler is recommended for samples collected from depths of greater than 5 feet.

4.3 When a Kemmerer sampler is used, the BOD sample bottle should be filled to overflowing. (Overflow for approximately 10 seconds). Outlet tube of Kemmerer should be inserted to bottom of BOD bottle. Care must be taken to prevent turbulence and the formation of bubbles when filling bottle.

4.4 The sample temperature should be recorded at time of sampling as precisely as required.

4.5 Do not delay the determination of dissolved oxygen in samples having an appreciable iodine demand or containing ferrous iron. If samples must be preserved either 4.5.1 or 4.5.2 below may be employed.

4.5.1 Add 2 ml of manganous sulfate reagent and then 2 ml of alkali azide reagent to the sample contained in the BOD bottle. Both reagents must be added well below the surface of the liquid. Stopper the bottle immediately and mix the contents thoroughly. The sample should be stored at the temperature of the collection water; or water sealed and kept at a temperature of 10 to 20°C, in the dark.

4.5.2 Add 0.7 ml of concentrated H_2SO_4 and 1 ml sodium azide solution (2 g NaN_3 in 100 ml distilled water) to the sample in the DO bottle. Store sample as in 4.5.1. Complete the procedure using 2 ml of manganous sulfate solution, 3 ml alkali iodide solution, and 2 ml of concentrated H_2SO_4.

4.6 If either preservation technique is employed, complete the analysis within 4-8 hours after sampling.

5. Apparatus

5.1 Sample bottles - 300 ml ±3 ml capacity BOD incubation bottles with tapered ground glass pointed stoppers and flared mouths.

5.2 Pipets - with elongated tips capable of delivering 2.0 ml ±0.1 ml of reagent.

6. Reagents

6.1 Manganous sulfate solution: Dissolve 480 g of manganous sulfate ($MnSO_4.4H_2O$) in distilled water and dilute to 1 liter.

6.1.1 Alternately, use 400 g of $MnSO_4.2H_2O$ or 364 g of $MnSO_4.H_2O$ per liter. When uncertainty exists regarding the water of crystallization, a solution of equivalent strength may be obtained by adjusting the specific gravity of the solution to 1.270 at 20°C.

6.2 Alkaline iodide solution: Dissolve 500 g of sodium hydroxide (NaOH) or 700 g of potassium hydroxide (KOH) and 135 g of sodium iodide (NaI) or 150 g of potassium iodide (KI) in distilled water and dilute to 1 liter. To this solution add 10 g of sodium azide (NaN_3) dissolved in 40 ml of distilled water.

6.3 Sulfuric acid, concentrated.

6.4 Starch solution: Prepare an emulsion of 10 g soluble starch in a mortar or beaker with a small quantity of distilled water. Pour this emulsion into 1 liter of boiling water, allow to boil a few minutes, and let settle overnight. Use the clear supernate. This solution may be preserved by the addition of 5 ml per liter of chloroform and storage in a 10°C refrigerator.

6.4.1 Dry, powdered starch indicators such as "thyodene" may be used in place of starch solution.

6.5 Potassium fluoride solution: Dissolve 40 g $KF.2H_2O$ in distilled water and dilute to 100 ml.

6.6 Sodium thiosulfate, stock solution, 0.75 N: Dissolve 186.15 g $Na_2S_2O_3.5H_2O$ in boiled and cooled distilled water and dilute to liter. Preserve by adding 5 ml chloroform.

6.7 Sodium thiosulfate standard titrant, 0.0375 N: Prepare by diluting 50.0 ml of stock solution to 1 liter. Preserve by adding 5 ml of chloroform. Standard sodium thiosulfate, exactly 0.0375 N is equivalent to 0.300 mg of DO per 1.00 ml. Standardize with 0.0375 N potassium biniodate.

6.8 Potassium biniodate standard, 0.375 N: Dissolve 4.873 g potassium biniodate, previously dried 2 hours at 103°C, in 1.0 liter of distilled water. Dilute 250 ml to 1.0 liter for 0.0375 N biniodate solution.

6.9 Standardization of 0.0375 N sodium thiosulfate: Dissolve 2 g ±1.0 g KI in 100 to 150 ml distilled water; add 10 ml of 10% H_2SO_4 followed by 20 ml standard potassium biniodate. Place in dark for 5 minutes, dilute to 300 ml, and titrate with the standard sodium thiosulfate titrant to a pale straw color. Add 1-2 ml starch solution and continue the titration drop by drop until the blue color disappears. Run in duplicate. Duplicate determinations should agree within ±0.05 ml.

7. Procedure

7.1 To the sample collected in the BOD incubation bottle, add 2 ml of the manganous sulfate solution followed by 2 ml of the alkali-iodide-azide reagent, well below the surface of the liquid; stopper with care to exclude air bubbles, and mix well by inverting the bottle several times. When the precipitate settles, leaving a clear supernatant above the manganese hydroxide floc, shake again. With estuarine-type waters, a minimum 2-minute period of contact with the precipitate rather than settling is sufficient. When settling has produced at least 100 ml of clear supernate, carefully remove the stopper and immediately add 2.0 ml of conc. H_2SO_4 (sulfamic acid packets, 3 g may be substituted for H_2SO_4)(1) by allowing the acid to run down the neck of the bottle, re-stopper, and mix by gentle inversion until the iodine is uniformly distributed throughout the bottle. Complete the analysis within 45 minutes.

---

(1) Kroner, R. C., Longbottom, J. E., Gorman, R., A Comparison of Various Reagents Proposed for Use in the Winkler Procedure for Dissolved Oxygen, PHS Water Pollution Surveillance System Applications and Development Report #12, Water Quality Section, Basic Data Branch, July 1964.

7.2 Transfer the entire bottle contents by inversion into a 500-ml wide mouth Erlenmeyer flask and titrate with 0.0375 N thiosulfate solution (where problems of stability arise, 0.0375 N PAO may be substituted as titrant)(1) to a pale straw color. Add 1-2 ml of starch solution or 0.1 g of powdered indicator and continue to titrate to the first disappearance of the blue color.

7.3 If ferric iron is present (100 to 200 ppm), add 1.0 ml of KF solution before acidification.

7.4 Occasionally, a dark brown or black precipitate persists in the bottle after acidification. This precipitate will dissolve if the solution is kept for a few minutes longer than usual or, if particularly persistent, a few more drops of H_2SO_4 will effect dissolution.

8. Calculation

8.1 Each ml of 0.0375 sodium thiosulfate titrant is equivalent to 1 mg/l DO when the entire bottle contents are titrated.

8.2 If the results are desired in milliliters of oxygen gas per liter at 0°C and 760 mm pressure, multiply mg/l DO by 0.698.

8.3 To express the results as percent saturation at 760 mm atmospheric pressure, the solubility data in Table 25 (Whipple & Whipple Table, p. 409, Standard Methods, 12th Edition) may be used. Equations for correcting the solubilities to barometric pressures other than mean sea level are given below the table.

8.4 The solubility of DO in distilled water at any barometric pressure, P (mm Hg), temperature, T°C, and saturated vapor pressure, μ (mm Hg), for the given T, may be calculated between the temperature of 0° and 30°C by:

$$\text{ml/l DO} = \frac{(P - U) \times 0.678}{35 + T}$$

and between 30° and 50°C by:

$$\text{ml/l DO} = \frac{(P - U) \times 0.827}{49 + T}$$

9. Precision and Accuracy

9.1 Exact data are unavailable on the precision and accuracy of this technique; however, reproducibility is approximately 0.2 ppm of DO at the 7.5 ppm level due to equipment tolerances and uncompensated displacement errors.

DISSOLVED OXYGEN

(Probe Method)

1. Scope and Application

1.1 The probe method for dissolved oxygen is recommended for those samples containing materials which interfere with the modified Winkler procedure such as sulfite, thiosulfate, polythionate, mercaptans, free chlorine or hypochlorite, organic substances readily hydrolyzed in alkaline solutions, free iodine, intense color or turbidity, biological flocs, etc.

1.2 The probe method is recommended as a substitute for the modified Winkler procedure in monitoring of streams, lakes, outfalls, etc., where it is desired to obtain a continuous record of the dissolved oxygen content of the water under observation.

1.3 The probe method may be used as a substitute for the modified Winkler procedure in BOD determinations where it is desired to perform non-destructive DO measurements on a sample.

1.4 The probe method may be used under any circumstances as a substitute for the modified Winkler procedure provided that the probe itself is standardized against the Winkler method on samples free of interfering materials.

1.5 The electronic readout meter for the output from dissolved oxygen probes is normally calibrated in convenient scales (0 to 10, 0 to 15, 0 to 20 mg/liter, for example) with a sensitivity of approximately 0.05 mg/liter.

Preceding page blank

2. Summary of Method

2.1 The most common instrumental probes for determination of dissolved oxygen in water are dependent upon electrochemical reactions. Under steady-state conditions, the current or potential can be correlated with DO concentrations. Interfacial dynamics at the probe-sample interface are a factor in probe response and a significant degree of interfacial turbulence is necessary. For precision performance, turbulence should be constant.

3. Sample Handling and Preservation

3.1 See 4.1, 4.2, 4.3, 4.4 under Modified Winkler Method.

4. Interferences

4.1 Dissolved organic materials are not known to interfere in the output from dissolved oxygen probes.

4.2 Dissolved inorganic salts are a factor in the performance of dissolved oxygen probe.

4.2.1 Probes with membranes respond to partial pressure of oxygen which in turn is a function of dissolved inorganic salts. Conversion factors for seawater and brackish waters may be calculated from dissolved oxygen saturation versus salinity data. Conversion factors for specific inorganic salts may be developed experimentally. Broad variations in the kinds and concentrations of salts in samples can make the use of a membrane probe difficult.

4.2.2 The thallium probe requires the presence of salts in concentrations which provide a minimum conductivity of approximately 200 micromhos.

4.3 Reactive compounds can interfere with the output or the performance of dissolved oxygen probes.

4.3.1 Reactive gases which pass through the membrane of membrane probes may interfere. For example, chlorine will depolarize the cathode and cause a high probe-output. Long-term exposures to chlorine will coat the anode with the chloride of the anode metal and eventually desensitize the probe. Alkaline samples in which free chlorine does not exist will not interfere. Hydrogen sulfide will interfere with membrane probes if the applied potential is greater than the half-wave potential of the sulfide ion. If the applied potential is less than the half-wave potential, an interfering reaction will not occur, but coating of the anode with the sulfide of the anode metal can take place.

4.3.2 Sulfur compounds (hydrogen sulfide, sulfur dioxide and mercaptans, for example) cause interfering outputs from the thallium probe. Halogens do not interfere with the thallium probe.

4.4 At low dissolved oxygen concentrations, pH variation below pH 5 and above pH 9 interfere with the performance of the thallium probe (approximately ±0.05 mg/l DO per pH unit). The performance of membrane probes is not affected by pH changes.

4.5 Dissolved oxygen probes are temperature sensitive, and temperature compensation is normally provided by the manufacturer. The thallium probe has a temperature coefficient of 1.9 m/°C. Membrane probes have a temperature coefficient of 4 to 6 percent/°C dependent upon the membrane employed.

5. Apparatus

5.1 No specific probe or accessory is especially recommended as superior. However, probes which have been evaluated or are in use and found to be reliable are the Weston & Stack DO Analyzer Model 30, the Yellow Springs Instrument (YSI) Model 54, and the Delta Scientific, Model 85.

6. Calibration

Follow manufacturer instructions.

7. Procedure

Follow manufacturer instructions.

8. Calculation

Follow manufacturer instructions.

9. Precision and Accuracy

Manufacturer's specification claim 0.1 mg/l repeatability with ±1% accuracy.

FLUORIDE

(Automated Complexone Method)

1. Scope and Application

1.1 This method is applicable to surface waters, domestic and industrial wastes, and saline waters. The applicable range of the method is 0.05 to 1.5 mg F/1. Twelve samples per hour can be analyzed.

2. Summary of Method

2.1 Fluoride ion reacts with the red cerous chelate of alizarin complexone. It is unlike other fluoride procedures in that a positive color is developed as contrasted to a bleaching action in previous methods.

3. Sample Handling and Preservation

3.1 No special requirements.

4. Interferences

4.1 Method is free from most anionic and cationic interferences, except aluminum, which forms an extremely stable fluoro compound, AIF_6^{-2}. This is overcome by treatment with 8-hydroxy quinoline to complex the aluminum and by subsequent extraction with chloroform.

5. Apparatus

   5.1 Technicon AutoAnalyzer Unit consisting of:

      5.1.1 Sampler I.

      5.1.2 Manifold.

      5.1.3 Proportioning pump.

      5.1.4 Continuous filter.

      5.1.5 Colorimeter equipped with 15 mm tabular flow cell and 650 mμ filters.

      5.1.6 Recorder equipped with range expander.

6. Reagents

   6.1 Sodium acetate solution: Dissolve 272 g (2 moles) of sodium acetate in distilled water and dilute to 1 liter.

   6.2 Acetic acid-8-hydroxyquinoline solution: Dissolve 6 g of 8-hydroxyquinoline in 34 ml of conc. acetic acid, and dilute to 1 liter.

   6.3 Chloroform: Analytical reagent grade.

   6.4 Ammonium acetate solution (6.7%): Dissolve 67 g of ammonium acetate in distilled water and dilute to 1 liter.

   6.5 Hydrochloric acid (2 N): Dilute 172 ml of conc. HCl to 1 liter.

   6.6 Lanthanum-alizarin fluoride blue solution: Dissolve 0.18 g of alizarin fluoride blue in a solution containing 0.5 ml of conc. ammonium hydroxide and 15 ml of 6.7% ammonium acetate. Add a solution that contains 41 g of anhydrous sodium carbonate and 70 ml of glacial acetic acid in 300 ml of distilled water. Add 250 ml of acetone. Dissolve 0.2 g of lanthanum oxide in 12.5 of 2 N hydrochloric acid and mix with above solution. Dilute to 1 liter.

6.7 Stock Solution: Dissolve 2.210 g of sodium fluoride in 100 ml of distilled water and dilute to 1 liter. 1 ml = 1.0 mg F.

6.8 Standard Solution: Dilute 10.0 ml of stock solution to 1 liter. 1 ml = 0.01 mg F.

6.8.1 Using standard solution, prepare the following standards in 100-ml volumetric flasks:

mg F/1	ml Standard Solution/100 ml
0.05	0.5
0.10	1.0
0.20	2.0
0.40	4.0
0.60	6.0
0.80	8.0
1.00	10.0
1.20	12.0
1.50	15.0

7. Procedure

7.1 Set up manifold as shown in Figure 1.

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.3 Place distilled water wash tubes in alternate openings in Sampler and set sample timing at 2.5 minutes.

7.4 Arrange fluoride standards in Sampler in order of decreasing concentration. Complete loading of Sampler tray with unknown samples.

7.5 Switch sample line from distilled water to Sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed fluoride standards against concentration values. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 In a single laboratory, using surface water samples at concentrations of 0.06, 0.15, 0.55, and 1.08 mg F/1, the standard deviation was ±0.018 (AQC Laboratory).

9.2 In a single laboratory, using surface water samples at concentrations of 0.14 and 1.25 mg F/1 recoveries were 89% and 102%, respectively (AQC Laboratory).

References

1. R. Greenhaigh and J. P. Riley, "The Determination of Fluorides in Natural Waters, with Particular Reference to Sea Water." Anal. Chim. Acta, 25, 179 (1961).

2. K. M. Chan and J. P. Riley, "The Automatic Determination of Fluoride in Sea Water and Other Natural Waters." Anal. Chim. Acta, 35, 365 (1966).

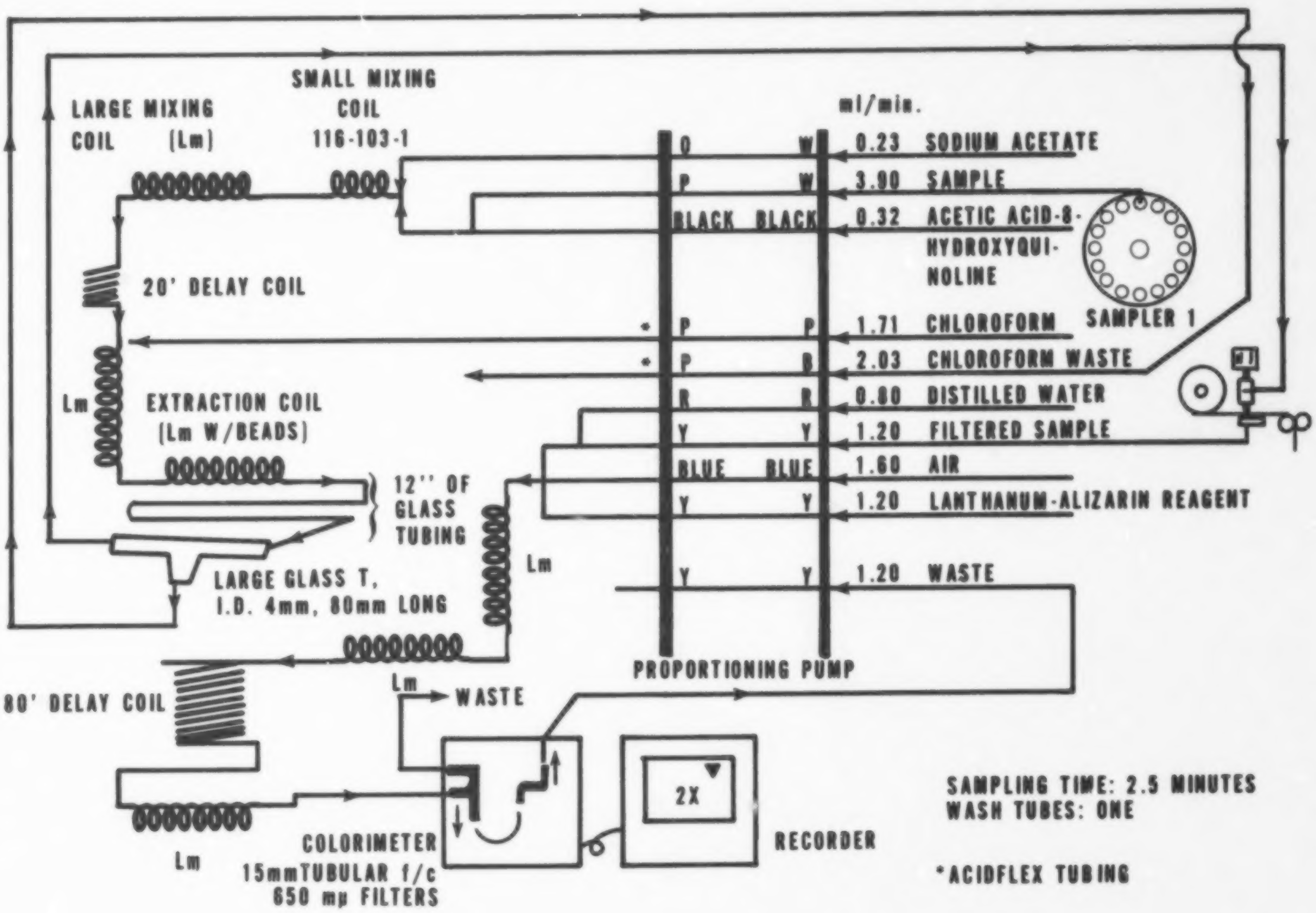

SMALL MIXING COIL 116-103-1
LARGE MIXING COIL (Lm)
20' DELAY COIL
Lm
EXTRACTION COIL (Lm W/BEADS)
12'' OF GLASS TUBING
LARGE GLASS T, I.D. 4mm, 80mm LONG
Lm
80' DELAY COIL
Lm
Lm
WASTE
COLORIMETER 15mmTUBULAR f/c 650 mμ FILTERS
2X
RECORDER
PROPORTIONING PUMP
ml/min.
O W 0.23 SODIUM ACETATE
P W 3.90 SAMPLE
BLACK BLACK 0.32 ACETIC ACID-8-HYDROXYQUINOLINE
* P P 1.71 CHLOROFORM
* P B 2.03 CHLOROFORM WASTE
R R 0.80 DISTILLED WATER
Y Y 1.20 FILTERED SAMPLE
BLUE BLUE 1.60 AIR
Y Y 1.20 LANTHANUM-ALIZARIN REAGENT
Y Y 1.20 WASTE
SAMPLER 1
SAMPLING TIME: 2.5 MINUTES
WASH TUBES: ONE
*ACIDFLEX TUBING

FIGURE 1. FLUORIDE MANIFOLD

FLUORIDE

(Specific Ion Electrode Method)

1. Scope and Application

1.1 This method is applicable to the measurement of fluoride in finished waters, natural waters, brines, and industrial waste waters and the need for distillation of the sample is eliminated.

1.2 Concentrations of fluoride from 0.1 up to 1000 mg/liter may be measured.

2. Summary of Method

2.1 The fluoride is determined potentiometrically using a specific ion fluoride electrode in conjunction with a standard single junction sleeve-type reference electrode and a pH meter having an expanded millivolt scale or a specific ion meter having a direct concentration scale for fluoride.

2.2 The fluoride electrode consists of a lazer-type doped lanthanum fluoride crystal across which a potential is developed by fluoride ions. The cell may be represented by Ag/Ag Cl, Cl^- (0.3), F^- (0.001) LaF_3/ test solution/SCE/.

3. Interferences

3.1 Extremes of pH interfere; sample pH should be between 5 and 9. Polyvalent cations of Si^{+4}, Fe^{+3} and Al^{+3} interfere by forming complexes with fluoride. The degree of interference depends

Preceding page blank

upon the concentration of the complexing cations, the concentration of fluoride and the pH of the sample. The addition of a pH 5.0 buffer (described below) containing a strong, chelating agent preferentially complexes aluminum (the most common interference), silicon, and iron, and eliminates the pH problem.

4. Sample Handling and Preservation

4.1 No special requirements.

5. Apparatus

5.1 Electrometer, (pH meter) with expanded mv scale or a specific ion meter such as the Orion 400 Series.

5.2 Fluoride Ion Activity Electrode, such as Orion No. 94-09.

5.3 Reference electrode, single junction, sleeve-type, such as Orion No. 90-01, Beckman No. 40454, or Corning No. 476010.

5.4 Magnetic Mixer, Teflon-coated stirring bar.

6. Reagents

6.1 Buffer solution, pH 5.0-5.5. To approximately 500 ml of distilled water in a one-liter beaker add 57 ml of glacial acetic acid, 58 g of sodium chloride and 2 g of CDTA(1).

---

(1) CDTA is the abbreviated designation of 1,2-cyclohexylene dinitrilo tetraacetic acid, produced by Mathieson, Coleman & Bell, Cat. No. P8661.

Stir to dissolve and cool to room temperature. Adjust pH of solution to between 5.0 and 5.5 with 5 N sodium hydroxide (about 150 ml will be required). Transfer solution to a 1-liter volumetric flask and dilute to the mark with distilled water. For work with brines, additional NaCl should be added to raise the chloride level to twice the highest expected level of chloride in the sample.

Note - CDTA replaces citric acid used in the original buffer formula. It is a strong chelating agent and more effectively ties up aluminum than the original citric acid.

6.2 Sodium fluoride, stock solution (1.0 ml = 0.01 mg F).

7. Calibration

7.1 Prepare a series of standards using the fluoride stock solution (1 ml = 0.01 mg F) in the range of 0 to 2.00 mg/liter by diluting appropriate volumes to 50 ml. The following series may be used:

Milliliters of Stock (1.0 ml = 0.01 mg/F)	Concentration when Diluted to 50 ml, mg F/liter
0.00	0.00
1.00	0.20
2.00	0.40
3.00	0.60
4.00	0.80
5.00	1.00
6.00	1.20
8.00	1.60
10.00	2.00

7.2 Calibration of Electrometer: Immerse the electrodes in each stock solution starting with the lowest concentration and measure the developed potential while mixing. The electrodes must remain in the solution for at least three minutes or until the reading has stabilized. Using semilogarithmic graph paper, plot the concentration of fluoride in mg/liter on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.

7.3 Calibration of a specific ion meter: Follow the directions of the manufacturer for the operation of the instrument.

8. Procedure

8.1 Place 50.0 ml of sample and 50.0 ml of buffer in a 150-ml beaker. Place on a magnetic stirrer and mix at medium speed. Immerse the electrodes in the solution and observe the meter reading while mixing. The electrodes must remain in the solution for at least three minutes or until the reading has stabilized. At concentrations under 0.5 ml/liter F, it may require as long as five minutes to reach a stable meter reading; higher concentrations stabilize more quickly. If a pH meter is used, record the potential measurement for each unknown sample and convert the potential reading to the fluoride ion concentration of the unknown using the standard curve. If a specific ion meter is used, read the fluoride level in the unknown sample directly in mg/l on the fluoride scale.

9. Precision and Accuracy

9.1 A synthetic sample prepared by the Analytical Reference Service, PHS, containing 0.85 mg/l fluoride and no interferences was analyzed by 111 different analysts; a mean of 0.84 mg/l with a standard deviation of ±0.030 was obtained.

9.2 On the same study, a synthetic sample containing 0.75 mg/l fluoride, 2.5 mg/l polyphosphate and 300 mg/l alkalinity, was analyzed by the same 111 analysts; a mean of 0.75 mg/l fluoride with a standard deviation of ±0.036 was obtained.

HARDNESS, TOTAL

(Automated Eriochrome BT Method)

1. Scope and Application

1.1 This automated method is applicable to surface and saline waters. The applicable range is 10 to 400 mg/l as $CaCO_3$. Approximately 12 samples per hour can be analyzed.

2. Summary of Method

2.1 The disodium magnesium EDTA exchanges magnesium on an equivalent basis for any calcium and/or other cations to form a more stable EDTA chelate than magnesium. The free magnesium reacts with Eriochrome Black T at a pH of 10 to give a red-violet complex. Thus, by measuring only magnesium concentration in the final reaction stream, an accurate measurement of total hardness is possible.

3. Sample Handling and Preservation

3.1 No special requirements.

4. Interferences

4.1 No significant interferences.

5. Apparatus

5.1 Technicon AutoAnalyzer consisting of:

5.1.1 Sampler I.

5.1.2 Continuous Filter.

Preceding page blank

5.1.3 Manifold.

5.1.4 Proportioning Pump.

5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 520 mμ filters.

5.1.6 Recorder equipped with range expander.

6. Reagents

6.1 Buffer: Dissolve 67.6 g NH_4Cl in 572 ml of NH_4OH and dilute to 1 liter.

6.2 Eriochrome Black T (or Calmagite): Dissolve 0.25 g in 500 ml of distilled water by stirring approximately 30 minutes on a magnetic stirrer. Filter.

6.3 Magnesium EDTA: Dissolve 0.2 g of MgEDTA in 1 liter of distilled water.

6.4 Stock Solution: Weigh 1.0 g of calcium carbonate (pre-dried at 105°C) into 500 ml Erlenmeyer flask; add 1:1 HCl until all $CaCO_3$ has dissolved. Add 200 ml of distilled water and boil for a few minutes. Cool, add a few drops of methyl red indicator, and adjust to the orange color with 3N NH_4OH and dilute to 1 liter. 1.0 ml = 1.0 mg $CaCO_3$.

6.4.1 Dilute each of the following volumes of stock solutions to 250 ml for appropriate standards:

Stock Solution, ml	$CaCO_3$, mg/l
2.5	10.0
5.0	20.0
10.0	40.0
15.0	60.0
25.0	100
35.0	140
50.0	200
75.0	300
100.0	400

7. Procedure

7.1 Set up manifold as shown in Figure 1.

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.3 Place distilled water wash tubes in alternate openings in Sampler and set sample timing at 2.5 minutes.

7.4 Arrange working standards in Sampler in order of decreasing concentration. Complete loading of Sampler tray with unknown samples.

7.5 Switch sample line from distilled water to Sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed standards against concentration values. Compute concentration of samples by comparing sample peak heights with standard curve.

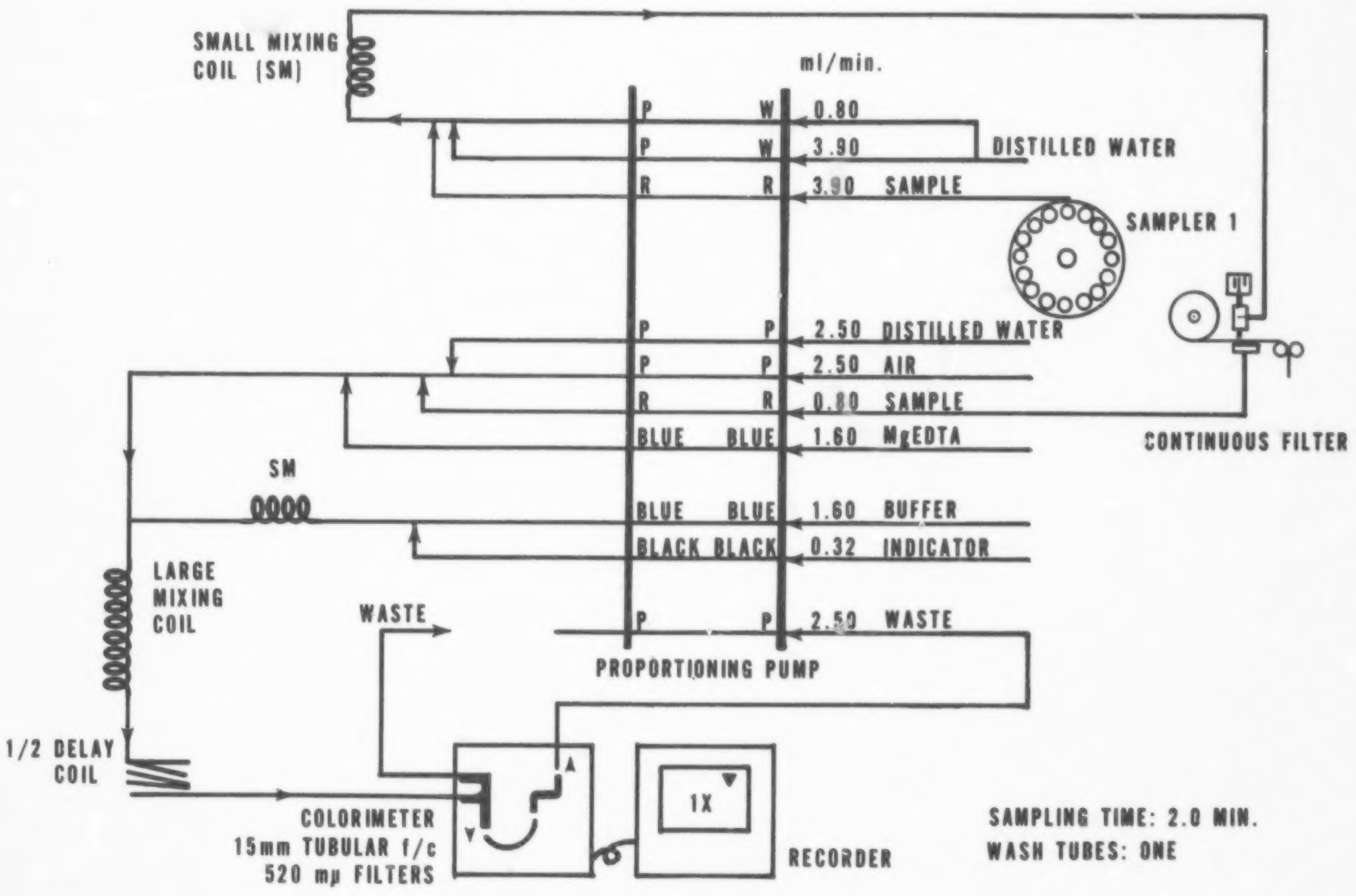
9. Precision and Accuracy

9.1 In a single laboratory (AQC), using surface water samples at concentrations of 19, 120, 385, and 366 mg/l as $CaCO_3$, the standard deviations were ±1.5, ±1.5, ±4.5, and ±5.0, respectively

9.2 In a single laboratory (AQC), using surface water samples at concentrations of 39 and 296 mg/l as $CaCO_3$, recoveries were 89% and 93%, respectively.

References

1. Technicon AutoAnalyzer Methodology, Bulletin No. 2, Technicon Controls, Inc., Chauncey, New York (July 1960).
2. Standard Methods, 12th Edition, p 147, American Public Health Association, New York, N.Y. (1965).


SMALL MIXING COIL (SM)
ml/min.
P W 0.80
P W 3.90 DISTILLED WATER
R R 3.90 SAMPLE
SAMPLER 1
P P 2.50 DISTILLED WATER
P P 2.50 AIR
R R 0.80 SAMPLE
BLUE BLUE 1.60 MgEDTA
CONTINUOUS FILTER
SM
BLUE BLUE 1.60 BUFFER
BLACK BLACK 0.32 INDICATOR
LARGE MIXING COIL
WASTE
P P 2.50 WASTE
PROPORTIONING PUMP
1/2 DELAY COIL
COLORIMETER
15mm TUBULAR f/c
520 mμ FILTERS
1X
RECORDER

SAMPLING TIME: 2.0 MIN.
WASH TUBES: ONE

FIGURE 1. HARDNESS MANIFOLD

METALS

(Atomic Absorption Methods)

1. Scope and Application

1.1 Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in surface waters, domestic and industrial wastes, and saline waters.

1.2 Detection limits, sensitivity and optimum ranges of the metals will vary with the various makes and models of satisfactory atomic absorption spectrophotometers. The data shown in Table 1, however, will provide the reader with some indication of the concentration ranges determinable. In the majority of instances the concentration range shown in the table may be extended much lower with scale expansion and conversely extended upwards by using a less sensitive wavelength. Sensitivity may also be extended through concentration of the sample or through solvent extraction techniques. Following are detection limits, sensitivities, and the optimum concentration ranges achieved directly on the sample using the Instrumentation Laboratories, Model IL-153 without scale expansion (Pos 2.5).

Preceding page blank

Metal	Detection Limit mg/l	Sensitivity mg/l	Optimum Concentration Range mg/l
Aluminum	0.1	0.4	10 - 1000
Arsenic	0.25	0.5	10 - 100
Cadmium	0.001	0.004	0.1 - 2
Calcium	0.003	0.07	1 - 200
Chromium	0.01	0.02	1 - 200
Copper	0.005	0.04	0.1 - 10
Iron	0.004	0.006	0.1 - 20
Lead	0.01	0.06	1 - 10
Magnesium	0.0005	0.005	0.01 - 2
Manganese	0.005	0.04	0.1 - 20
Potassium	0.005	0.01	0.01 - 2
Silver	0.01	0.05	0.1 - 20
Sodium	0.001	0.003	1 - 200
Zinc	0.005	0.02	0.1 - 2

2. Summary of Method

2.1 Atomic absorption spectroscopy is similar to flame emission photometry in that a sample is aspirated into a flame and atomized. Flame photometry, however, measures the amount of light emitted, whereas, in atomic absorption spectrophotometry a light beam is directed through the flame into a monochromator, and onto a detector that measures the amount of light absorbed. In many instances absorption is more sensitive because it depends upon the presence of free unexcited atoms and generally the ratio of unexcited to excited atoms at a given moment is very high. Since the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

2.2 Although methods have been reported for the analysis of solids by atomic absorption spectroscopy the technique generally is limited to metals in solution or solubilized through some form of sample processing. Thus it is a relatively simple matter to determine metals in the soluble fraction by aspirating a filtered portion of the water sample.

2.21 In those instances where complete characterization of a sample is desired, the suspended material must also be analyzed. This may be accomplished by filtration and acid digestion of the suspended material. Metalic constituents in this acid digest are subsequently determined and the sum of the dissolved plus suspended concentrations will then provide the total concentrations present

2.22 The sample may also be treated with acid before filtration to measure what may be termed "extractable" concentrations.

3. Definition Of Terms

3.1 Sensitivity: is the concentration in milligrams of metal per liter that produces an absorption of 1%.

3.2 Detection Limit: is defined as the concentration that produces absorption equivalent to twice the magnitude of the fluctuation in the background (zero absorption).

3.3 Dissolved: those constituents which will pass through a 0.45 μ membrane filter.

3.4 Suspended: those constituents which are retained by a 0.45 μ membrane filter.

3.5 Total: concentration is the sum of the concentrations in the dissolved and suspended fraction.

3.6 Extractable: the extractable fraction is the dissolved concentrations plus that quantity adsorbed on the surface of the silt particles that is soluble in hot dilute mineral acids.

4. Sample Handling and Preservation

4.1 For the determination of trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. For liquid samples, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. The sample bottle should be thoroughly washed with detergent and tap water; rinsed with chromic acid, tap water, nitric acid, tap water and finally distilled water in that order. After collection of the sample the analyst must decide on the type of desired data, ie., dissolved, suspended, total or extractable, before proceeding with the sample handling.

4.11 For the determination of soluble constituents the sample should be filtered through a 0.45 μ membrane filter as soon as practicable after collection. Use the first 50-100 ml to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with 1:1 redistilled nitric acid (3 ml per liter). Normally this amount of acid will lower the pH to 2 or 3 and should be sufficient to preserve the sample indefinitely. Analyses performed on a sample so treated shall be reported as "dissolved" concentrations.

4.12 For the determination of suspended metals a representative volume of sample should be filtered through a 0.45 μ membrane filter. When considerable sediment is present, as little as 100 ml of a well shaken sample is filtered.

Record the volume filtered and transfer the membrane filter containing the sediment to a 250 ml Griffin beaker and add 3 ml distilled HNO_3. Cover the beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane. Increase the temperature of the hot-plate and digest the material. When the acid has evaporated, cool the beaker and watch glass and add another 3 ml of distilled HNO_3.

Cover and continue heating until the digestion is complete, generally indicated by a light colored residue. Add distilled 1:1 HCl (2 ml) to the dry residue and again warm the beaker gently to dissolve the material. Wash down the watch glass and beaker walls with distilled water and filter the sample to remove silicates and other insoluble material that would clog the atomizer. Adjust the volume to some predetermined value based on the expected concentrations of trace metals present. This volume will vary depending on the metal to be determined. The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended". STORET parameter numbers for reporting this type of data are currently not available.

4.13 To determine metals soluble in diluted hot HCl - HNO_3, acidify the entire sample at the time of collection with redistilled HNO_3, 5 ml/l. At the time of analysis the sample is mixed and a 100-ml aliquot transferred to a beaker or flask. Five ml of redistilled hydrochloric acid is added and the sample heated for 15 minutes on a steam bath or hot plate. After this digestion period the sample is filtered and the volume adjusted to 100 ml. The sample is then ready for analysis.

The data so obtained are significant in terms of "total" metals in the sample, with the reservation that something less than "total" is actually measured. Concentrations of metal found, especially in heavily silted samples, will be substantially higher than data obtained on only the soluble fraction. STORET parameter numbers for the storage of this type data are not available.

5. Interferences

5.1 The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and results from lack of absorption of atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or because the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome the phosphate interference in the magnesium determination. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium.

5.11 Chemical interferences may also be eliminated by separating the metal from the interfering material. While complexing agents are usually employed to increase the sensitivity of the analysis they may also be used to eliminate or reduce interferences.

6. Apparatus

6.1 Atomic absorption spectrophotometer: Instrumentation Laboratory, Model IL-153 or equivalent. A satisfactory instrument will have an energy source, an atomizer burner system, a monochrometer, and a detector.

6.2 Burner: A Boling burner is recommended for most aqueous solutions. A premix burner is used for organic solvents. For certain elements the nitrous oxide burner is preferred.

6.3 Volumetric flasks; 200 ml, for extraction with organic solvents.

6.4 Glassware: All glassware, including sample bottles, should be washed with detergent, rinsed with tap water, chromic acid, tap water, 1:1 nitric acid, tap water and distilled water in that order.

6.5 Borosilicate glass distillation apparatus.

7. Reagents

7.1 Deionized distilled water: Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized distilled water for the preparation of all reagents, calibration standards, and as dilution water.

7.2 Nitric acid (conc): Distill reagent grade nitric acid in a borosilicate glass distillation apparatus. Prepared a 1:1 dilution with deionized distilled water.

7.3 Hydrochloric acid (1:1): Prepare a 1:1 solution of reagent grade hydrochloric acid and distilled water. Distill this mixture from a borosilicate glass distillation apparatus.

7.4 Stock metal solutions: Prepare as directed in 8.1 and under the individual metal procedures.

7.5 Standard metal solutions: Prepare a series of standards of the metal by dilution of the appropriate stock metal solution to cover the concentration range desired.

7.6 Fuel and oxidant: Commercial grade acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or from a cylinder of compressed air. Reagent grade nitrous oxide is also required for certain determinations.

7.7 Special reagents for the extraction procedure

a. Ammonium pyrrolidine dithiocarbamate solution (APDC): Dissolve 1g APDC in 100 ml of deionized distilled water. Prepare fresh before use.

b. Bromphenol blue indicator solution: Dissolve 0.1g bromphenol blue in 100 ml 50% ethanol.

c. Hydrochloric acid, 0.3N: Mix 25 ml conc. HCl with deionized distilled water and dilute to 1 liter.

d. Methyl isobutyl ketone (MIBK):

Ammonium pyrrolidine dithiocarbamate (APDC) may be obtained commercially from Fisher Scientific Company (Cat. No. A-182), K and K Labs Inc. or Eastman Kodak.

e. Sodium hydroxide, 2.5N:

Dissolve 10 g NaOH in deionized distilled water and dilute to 100 ml.

8. Preparation of Standards and Calibration

8.1 Stock solutions are prepared from high purity metals, oxides or nonhygroscopic reagent grade salts using redistilled nitric or hydrochloric acids. Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared at concentrations of 1000 mg/l.

8.2 Standard solutions are prepared by diluting the stock metal solutions at the time of analysis. For best results, calibration standards should be prepared fresh each time an analysis is to be made and discarded after use. Prepare a blank and calibration standards in graduated amounts in the appropriate range. As the filtered samples are preserved with redistilled nitric acid (3 ml (1:1) per liter) the acid strength of the calibration standards should be similarly adjusted. Beginning with the blank and working toward the highest standard, aspirate the solutions and record the readings. Repeat the operation with both the calibration standards and the samples a sufficient number of times to secure a reliable average reading for each solution.

8.3 For those instruments which do not read out directly in concentration a calibration curve is prepared to cover the appropriate concentration range. Usually, this means the preparation of standards which produce an absorption of 0 to 80 percent. The correct method for plotting data derived from an atomic absorption instrument equipped with a linear readout system is to convert percent absorption to absorbance and plot the absorbance against concentration. The following relationship is used to convert absorption values to absorbance:

absorbance = log (100/% T) = 2 - log % T

where % T = 100 - % absorption

As the curves are frequently nonlinear, especially at high absorption values, the number of standards should be increased in that portion of the curve.

9. General Procedure for Analysis by Atomic Absorption

9.1 Differences between the models of satisfactory atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the manufacturer's operating instructions for his particular instrument. In general, after choosing the correct hollow cathode lamp for the analysis, the lamp should be allowedto warm up for a minimum of 15 minutes. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, adjust the hollow cathode current according to the manufacturer's recommendation, light the flame and regulate the flow of fuel and oxidant, adjust the burner for maximum percent absorption and stability and balance the photometer. Run a series of standards of the element under analysis and construct working curves by plotting the concentrations of the standards against the absorbance. For those instruments which read directly in concentration set the curve corrector to read out the proper concentration. Aspirate the samples and determine the concentrations either directly or from the calibration curve. For best results run standards each time a sample or series of samples are run.

9.2 Special Extraction Procedure: When the concentration of the metal is not sufficiently high to determine directly, or when considerable dissolved solids are present in the sample, certain of the metals may be chelated and extracted with organic solvents. Ammonium pyrrolidine dithiocarbamate (APDC) is widely used for this purpose and is particularly useful for zinc, cadmium, iron, manganese, copper, silver, lead and chromium^{+6}. The most frequently used organic solvent for APDC is methyl isobutyl ketone (MIBK). Apart from the fact that the solvent should extract the chelate, it should burn and provide a stable flame. In addition, the physical properties of the solvent such as viscosity, surface tension, boiling point, and mutual solubility in an aqueous medium must be taken into account. It should not produce toxic products during combustion or give a high background in the flame.

9.21 Extraction Procedure with APDC

a. Pipet a volume of sample (100 ml max.) into a 200 ml volumetric flask and adjust the volume to 100 ml with deionized distilled water.

b. Prepare a blank and sufficient standards in the same manner and adjust the volume of each to approximately 100 ml with deionized distilled water.

c. Add 2 drops of bromphenol blue indicator solution.

d. Adjust the pH of the sample by dropwise addition of 2.5N NaOH until a blue color persists. Add 0.3N HCl dropwise until the blue color just disappears in both standards and samples. Then add 2.0 ml of 0.3N HCl in excess.

e. Add 2.5 ml fresh APDC solution and mix.

f. Add 10.0 ml MIBK and shake vigorously for 1 minute.

g. Allow the layers to separate and add deionized distilled water until the ketone layer is completely in the neck of the flask.

h. Aspirate the ketone layer and record the scale readings for each standard and sample against the prepared blank. Repeat and average the duplicate results. Plot a calibration curve in μg metal vs. absorbance.

Note:

When aspirating organic solvents the fuel-to-air ratio should be reduced as the burning of the organic solvent contributes to the fuel supply. When adjusting the fuel-to-air ratio of the gas mixture at the burner, begin with the settings recommended by the manufacturer. Gradually reduce the fuel flow while the organic solvent is being aspirated until the flame is as blue as possible. Care should be taken that the flame does not lift off the burner producing an undesirable luminescent flame.

10. Calculation

10.1 Direct determination: Read the metal value in mg/l from the calibration curve or directly from the readout system of the instrument.

mg/l metal in sample = (mg/l of metal in the aliquot) x D

$$\text{where } D = \frac{\text{ml of aliquot + ml of deionized distilled water}}{\text{ml of aliquot}}$$

10.2 Extracted samples: Read the metal value in μg from the extracted calibration curve or from the readout system of the instrument.

$$\text{mg/l metal in sample} = \frac{\mu\text{g metal in aliquot}}{\text{ml of aliquot}}$$

11. Precision and Accuracy

11.1 Three synthetic unknown samples containing varying concentrations of cadmium, chromium, copper, iron, lead, magnesium, manganese, silver, and zinc were analyzed in 59 laboratories with the results indicated in Table 2. (Analytical Reference Service PHS)

Table 2

Precision and Accuracy Data for Atomic Absorption Methods

Metal	Metal Concentration, µg/l	Relative Error, percent	Relative Standard Deviation, percent
Direct determination			
Cadmium	50	8.15	21.62
Chromium	50	2.29	26.44
Copper	1000	3.42	11.23
Iron	300	0.64	16.53
Magnesium	200	6.30	10.49
Manganese	50	6.00	13.50
Silver	50	10.57	17.47
Zinc	500	0.41	8.15
Extracted samples			
Cadmium	10	3.03	72.77
Lead	50	19.00	23.46

Aluminum - Standard Conditions

Optimum Concentration Range 10-1000 mg/l using the 3092 A line

Sensitivity 0.4 mg/l

Detection Limit 0.1 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.000 gram of aluminum metal (analytical reagent grade). Add 15 ml of concentrated HCl to the metal in a covered beaker and warm gently. When solution is complete, transfer quantitatively to a 1 liter volumetric flask and make up to volume with distilled water. One ml equals 1 mg Al.
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Maintain an acid strength of 0.15% nitric acid in all calibration standards.

Instrumental Parameters (General)

1. Aluminum hollow cathode lamp
2. Wavelength: 3092 A
3. Type of burner: Nitrous oxide
4. Fuel: Acetylene
5. Oxidant: Nitrous oxide
6. Type of flame: Fuel rich
7. Photomultiplier tube: IP-28

Notes

1. The following lines may also be used

   3082 A Relative Sensitivity 1

   3962 A Relative Sensitivity 2

   3944 A Relative Sensitivity 2.5

Arsenic - Standard Conditions

Optimum Concentration Range 10-100 mg/l using the 1937 A line

Sensitivity 0.5 mg/l

Detection Limit 0.25 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.320 grams of arsenic trioxide (As_2O_3, analytical reagent grade) in a small quantity of distilled water in which a pellet of NaOH has previously been dissolved. When solution is complete acidify with HCl and make up to 1 liter with distilled water. One ml equals 1 mg As (1000 mg/l.
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Do not acidify with nitric acid.

Instrumental Parameters (General)

1. Arsenic hollow cathode lamp
2. Wavelength: 1937 A
3. Type of burner: Boling
4. Fuel: Hydrogen
5. Oxidant: Argon
6. Type of flame: Fuel rich
7. Photomultiplier tube: R-106

Notes

1. The R-106 photomultiplier tube is more sensitive to UV light and therefore is suggested in place of the IP-28 phototube.
2. The presence of nitric acid causes interference in the argon-hydrogen system, therefore a separate sample preserved with HCl should be analyzed.
3. Samples high in total salt content (above 1%) will produce an apparent absorption at the 1937 A arsenic line even when the element is absent. It is necessary, therefore, to correct absorption readings at low absorptions by subtracting the signal obtained at a neighboring, nonabsorbing line.
4. The high-solids burner is reported to give lower detection limits.

Cadmium - Standard Conditions

Optimum Concentration Range 0.1-1 mg/l using the 2288 A line

Sensitivity 0.004 mg/l

Detection Limit 0.001 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.142 gram of cadmium oxide (CdO, analytical reagent grade) and dissolve in 5 ml redistilled HNO_3. Dilute to 1 liter with distilled water. One ml equals 1 mg Cd.
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Maintain an acid strength of 0.15% nitric acid in all calibration standards.

Instrumental Parameters (General)

1. Cadmium hollow cathode lamp
2. Wavelength: 2288 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing
7. Photomultiplier tube: IP-28

Calcium - Standard Conditions

Optimum Concentration Range 1.0-200 mg/l using the 4227 A line

Sensitivity 0.07 mg/l

Detection Limit 0.003 mg/l

Preparation of Standard Solution

1. Stock Solution: Suspend 1.250 grams of $CaCO_3$ (analytical reagent grade), dried at 180°C for 1 hour before weighing, in distilled water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1000 ml with distilled water. One ml equals 0.5 mg of Ca (500 mg/l).
2. Lanthaum chloride solution: Dissolve 29 g of La_2O_3, slowly and in small portions, in 250 ml concentrated HCl. (Caution! Reaction is violent) and dilute to 500 ml with distilled water.
3. Prepare dilutions of the stock calcium solution to be used as calibration standards at the time of analysis. To each calibration standard solution, add 1.0 ml of $LaCl_3$ solution for each 10 ml of volume of working standard, ie., 20 ml working standard + 2 ml $LaCl_3$ = 22 ml.

Instrumental Parameters (General)

1. Calcium hollow cathode lamp
2. Wavelength: 4227 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Reducing
7. Photomultiplier tube: IP-28

Notes

1. Phosphate, sulfate and aluminum interfere but are masked by the addition of lanthanum. Since low calcium values result if the pH of the sample is above 7, both standards and samples are prepared in dilute hydrochloric acid solution. Concentrations of magnesium greater than 1000 mg/l also cause low calcium values. Concentrations of up to 500 mg/l each of sodium, potassium and nitrate cause no interference.
2. Anionic chemical interferences can be expected if lanthanum is not used in samples and standards.
3. The nitrous oxide-acetylene flame will provide two to five times greater sensitivity and freedom from chemical interferences. Ionization interferences should be controlled by adding a large amount of alkali to the samples and standards. The analysis appears to be free from chemical supressions in the nitrous oxide - acetylene flame.
4. The 2399 A line may also be used. This line has a sensitivity of 20 mg/l.

Chromium - Standard Conditions

Optimum Concentration Range 1.0-200 mg/l using the 3579 A line

Sensitivity 0.02 mg/l

Detection Limit 0.01 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.923 gram of chromium trioxide (CrO_3, reagent grade) in distilled water. When solution is complete acidify with redistilled HNO_3 and dilute to 1 liter with distilled water. One ml equals 1 mg chromium.
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Maintain an acid strength of 0.15% nitric acid in all calibration standards.

Instrumental Parameters (General)

1. Chromium hollow cathode lamp
2. Wavelength: 3579 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Slightly fuel rich
7. Photomultiplier tube: IP-28

Notes

1. The following wavelengths may also be used

   3605 A Relative Sensitivity 1.2
   3593 A Relative Sensitivity 1.4
   4254 A Relative Sensitivity 2
   4274 A Relative Sensitivity 3
   4289 A Relative Sensitivity 4

2. The determination of chromium requires a rich acetylene flame. The absorption is very sensitive to the fuel-to-air ratio.

3. The absorption of chromium is suppressed by iron and nickel. If the analysis is performed in a lean flame the interference can be lessened but the sensitivity will also be reduced. The interference does not exist in a nitrous oxide - acetylene flame.

Copper - Standard Conditions

Optimum Concentration Range 0.1-10 mg/l using the 3247 A line

Sensitivity 0.04 mg/l

Detection Limit 0.005 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.00 gram of electrolytic copper (analytical reagent grade). Dissolve in 5 ml redistilled HNO_3 and make up to 1 liter with distilled water. Final concentration is 1 mg Cu per ml (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Maintain an acid strength of 0.15% nitric acid in all calibration standards.

Instrumental Parameters (General)

1. Copper hollow cathode lamp
2. Wavelength: 3247 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing
7. Photomultiplier tube: IP-28

Notes

1. For copper concentrations below 0.05 mg/1, the extraction procedure is suggested.
2. Copper atoms are distributed over a wider area in laminar flow-flames than that normally found. Consequently, the burner parameters are not as critical as for most other elemental determinations.
3. Because of the spectral intensity of the 3247 A line, the P.M. tube may become saturated. If this situation occurs the current should be decreased.
4. Numerous absorption lines are available for the determination of copper. By selecting a suitable absorption wavelength, copper samples may be analyzed over a very wide range of concentration. The following lines may be used.

    3264 A Relative Sensitivity 2

    2178 A Relative Sensitivity 4

    2165 A Relative Sensitivity 7

    2181 A Relative Sensitivity 9

    2225 A Relative Sensitivity 20

    2024 A Relative Sensitivity 20

    2492 A Relative Sensitivity 90

Iron - Standard Conditions

Optimum Concentration Range 0.1-20 mg/l using the 2483 A line

Sensitivity 0.006 mg/l

Detection Limit 0.004 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.000 gram of pure iron wire (analytical reagent grade) and dissolve in 5 ml redistilled HNO_3, warming if necessary. When solution is complete make up to 1 liter with distilled water. One ml equals 1 mg Fe.
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Maintain an acid strength of 0.15% nitric acid in all calibration standards.

Instrumental Parameters (General)

1. Iron hollow cathode lamp
2. Wavelength: 2483 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing
7. Photomultiplier tube: IP-28

Notes

1. The following lines may also be used

   2488 A Relative Sensitivity 2

   2522 A Relative Sensitivity 2

   2719 A Relative Sensitivity 4

   3021 A Relative Sensitivity 5

   2527 A Relative Sensitivity 6

   2721 A Relative Sensitivity 9

   3720 A Relative Sensitivity 10

   2967 A Relative Sensitivity 12

   3860 A Relative Sensitivity 20

   3441 A Relative Sensitivity 30

2. Absorption is strongly dependent upon the lamp current.
3. Better signal-to-noise can be obtained from a neon-filled hollow cathode lamp than from an argon-filled lamp.

Lead - Standard Conditions

Optimum Concentration Range 1-10 mg/l using the 2170 A line

Sensitivity 0.06 mg/l

Detection Limit 0.01 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.599 gram of analytical reagent grade lead nitrate ($Pb(NO_3)_2$,) and dissolve in redistilled water. When solution is complete acidify with 10 ml redistilled HNO_3 and dilute to 1 liter with distilled water. One ml equals 1 mg Pb (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Maintain an acid strength of 0.15% nitric acid in all calibration standards.

Instrumental Parameters (General)

1. Lead hollow cathode lamp
2. Wavelength: 2170
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Slightly oxidizing
7. Photomultiplier tube: IP-28

Notes

1. The analysis of this metal is exceptionally sensitive to turbulence and absorption bands in the flame. Therefore, some care should be taken to position the light beam in the most stable, center portion of the flame. To do this, first adjust the burner to maximize the absorbance reading with a lead standard. Then, aspirate a water blank and make minute adjustments in the burner alignment to minimize the signal.
2. Better analytical results with the 2170 A line may be obtained by using a R-106 photomultiplier tube which is more sensitive to UV light.
3. For lead concentrations below 0.2 mg/l, the extraction procedure is suggested.
4. The following lines may also be used

   2833 A Relative Sensitivity 2
   2614 A Relative Sensitivity 500
   3683 A Relative Sensitivity 900

Magnesium - Standard Conditions

Optimum Concentration Range 0.01-2 mg/l using the 2852 A line

Sensitivity 0.005 mg/l

Detection Limit 0.0005 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 0.829 g of magnesium oxide, MgO (analytical reagent grade) in 10 ml of redistilled HNO_3 and dilute to 1 liter with distilled water. One ml equals 0.50 Mg.
2. Lanthanum chloride solution: Dissolve 29 g of La_2O_3, slowly and in small portions in 250 ml concentrated HCl. (Caution! Reaction is violent) and dilute to 500 ml with distilled water.
3. Prepare dilutions of the stock magnesium solution to be used as calibration standards at the time of analysis. To each calibration standard solution, add 1.0 ml of $LaCl_3$ solution for each 10 ml of volume of working standard, ie., 20 ml working standard + 2 ml $LaCl_3$ = 22 ml.

Instrumental Parameters (General)

1. Magnesium hollow cathode lamp
2. Wavelength: 2852 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Reducing
7. Photomultiplier tube: IP-28

Notes

1. Analytical sensitivity decreases with increased lamp current.
2. The interference caused by aluminum at concentrations greater than 2 mg/l is masked by addition of lanthanum. Since low magnesium values result if the pH of the samples is above 7, both standards and samples are prepared in dilute hydrochloric acid. Sodium, potassium and calcium cause no interference at concentrations less than 400 mg/l.
3. Because of the spectral intensity of the 2852 line, the P.M. tube may become saturated. If this situation occurs, the current should be decreased.
4. The following lines may also be used

2025 A	Relative Sensitivity	250
7025 A	Relative Sensitivity	250
2796 A	Relative Sensitivity	1000

5. To cover the range of magnesium values normally observed in surface waters (0.1-20 mg/l), it is suggested that the burner be rotated 55°.

Manganese - Standard Conditions

Optimum Concentration Range 0.1-20 mg/l using the 2795 A line

Sensitivity 0.04 mg/l

Detection Limit 0.005 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.583 gram of analytical reagent grade manganese dioxide, MnO_2 and dissolve in 10 ml of HCl. When solution is complete dilute to 1 liter with distilled water. One ml equals 1 mg Mn.
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Maintain an acid strength of 0.15% nitric acid in all calibration standards.

Instrumental Parameters (General)

1. Manganese hollow cathode lamp
2. Wavelength: 2795 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing
7. Photomultiplier tube: IP-28

Notes

1. For manganese concentrations below 0.01 mg/l, the extraction procedure is suggested. The extraction is carried out at pH 4.5-5.
2. Analytical sensitivity is somewhat dependent on lamp current.

Potassium - Standard Conditions

Optimum Concentration Range 0.01-2 mg/l using the 7665 A line

Sensitivity 0.01 mg/l

Detection Limit 0.005 mg/l

Preparation of Standard Solutions

1. Stock Solution: Dissolve 0.1907 grams of KCl (analytical reagent grade), dried at 110°C, in distilled water and make up to 1 liter. One ml equals 0.10 mg of potassium (100 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis.

Instrumental Parameters (General)

1. Potassium hollow cathode lamp
2. Wavelength: 7665 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Slightly oxidizing
7. Photomultiplier tube: IP-21

Notes

1. If an IP-21 photodetector tube is not available, the IP-28 may be used. This will result in some loss of sensitivity.
2. The Osram potassium vapor-discharge lamp may also be used in the Perkin-Elmer 303. In this case the lamp current should be 350 ma or the optimum operating current.
3. Sodium may interfere if present at much higher levels than the potassium. This effect can be avoided by approximately matching the sodium content of the potassium standards with that of the sample.
4. Potassium absorption is enhanced in the presence of Na, Li and Cs, especially in a high-temperature flame. This enhancement effect of sodium can be eliminated by changing the burner height and the type of flame used. The burner assembly is set approximately 0.05 cm below the optical light path so that the optical light path is sliced at the bottom by the burner head. A fuel-rich flame is used (303-burner, airflow 7.5, acetylene flow 9.0).
5. The 4044 A line may also be used. This line has a sensitivity of 5 mg/l for 1% absorption.
6. To cover the range of potassium values normally observed in surface waters (0.1-20 mg/l), it is suggested that the burner be rotated 75°.

Silver - Standard Conditions

Optimum Concentration Range 0.1-20 mg/1 using the 3281 A line

Sensitivity 0.05 mg/1

Detection Limit 0.01 mg/1

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.575 g of $AgNO_3$ (analytical reagent grade) in distilled water, add 10 ml HNO_3 and make up to 1 liter. One ml equals 1 mg of silver.
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Maintain an acid strength of 0.15% HNO_3 in all calibration standards.

Instrumental Parameter (General)

1. Silver hollow cathode lamp
2. Wavelength: 3281 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing
7. Photomultiplier tube: IP-28

Notes

1. The 3382 A line may also be used. This line has a relative sensitivity of 3.
2. Silver nitrate standards are light sensitive. Dilutions of the stock solution should be discarded after use as concentrations below 10 mg/l are not stable over long periods of storage.

Sodium - Standard Conditions

Optimum Concentration Range 1.0-200 mg/l using the 3302 A line

Sensitivity 0.003 mg/l

Detection Limit 0.001 mg/l

Preparation of Standard Solutions

1. Stock Solution: Dissolve 2.542 g of NaCl (analytical reagent grade), dried at 140°C, in distilled water and make up to 1 liter. One ml equals 1 mg of sodium.
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis.

Instrumental Parameters (General)

1. Sodium hollow cathode lamp
2. Wavelength: 3302 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing
7. Photomultiplier tube: IP-28

Notes

1. For the Perkin-Elmer instrument the "290" burner is used to increase the concentration range of sodium using the most sensitive line 5890. The burner is installed perpendicular (rotated 90°) to the light path. The upper concentration limit is 60 mg/l without sample dilution.
2. The 3302 A resonance line of sodium yields a sensitivity of about 5 mg/l sodium for 1% absorption and provides a convenient way to avoid the need to dilute more concentrated solutions of sodium.
3. Low-temperature flames increase sensitivity by reducing the extent of ionization of this easily ionized metal.
4. For more sensitivity the IP-21 photomultiplier tube and the 5890 A line may be used to extend the range to 0.005-0.2 mg/l.

Zinc - Standard Conditions

Optimum Concentration Range 0.1-2 mg/1 using the 2139 A line

Sensitivity 0.02 mg/1

Detection Limit 0.005 mg/1

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.00 gram of analytical reagent grade zinc metal and dissolve cautiously in 10 ml NHO_3. When solution is complete make up to 1 liter with distilled water. One ml equals 1 mg Zn.
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Maintain an acid strength of 0.15% HNO_3 in all calibration standards.

Instrumental Parameters (General)

1. Zinc hollow cathode lamp
2. Wavelength: 2139 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing
7. Photomultiplier tube: IP-28

Notes

1. High levels of silicon may interfere.
2. The air-acetylene flame absorbs about 25% of the energy at the 2139 A line.
3. The sensitivity may be increased by the use of low-temperature flames.

NITROGEN-AMMONIA

(Distillation Procedure)

1. Scope and Application

1.1 This distillation method covers the determination of ammonia-nitrogen, exclusive of total Kjeldahl nitrogen, in surface waters, domestic and industrial wastes, and saline waters. It is the method of choice where economics and sample-load do not warrant the use of automated equipment.

1.2 The method covers the range from about 0.05 to 1.0 mg/l NH_3/N per liter for the colorimetric procedures and from 1.0 to 25 mg/l for the titrimetric procedure.

1.3 This method is described for macro glassware; however, micro distillation equipment may also be used.

2. Summary of Method

2.1 The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is then distilled into a solution of boric acid. The ammonia in the distillate can be determined either colorimetrically by nesslerization or titrimetrically with standard sulfuric acid with the use of a mixed indicator, the choice between these two procedures depending on the concentration of the ammonia.

3. Sample Handling and Preservation

3.1 Until more conclusive data is obtained samples may be preserved by addition of 40 mg $HgCl_2$ and stored at 4°C. If only ammonia is to be determined on the sample it may be preserved with 1.0 ml of concentrated H_2SO_4 per liter and stored at 4°C.

4. Interferences

4.1 A number of aromatic and aliphatic amines, as well as other compounds, both organic and inorganic, will cause turbidity upon the addition of Nessler reagent, so direct nesslerization (i.e., without distillation), has been discarded as an official method.

4.2 Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at the pH of 9.5 at which distillation is carried out. Volatile alkaline compounds such as hydrazine will influence the titrimetric results. Some volatile compounds, such as certain ketones, aldehydes, and alcohols, may cause an off-color upon nesslerization in the distillation method. Some of these, such as formaldehyde, may be eliminated by boiling off at a low pH prior to distillation and nesslerization.

4.3 Residual chlorine must also be removed by pre-treatment of the sample with sodium thiosulfate before distillation.

4.4 If the sample has been preserved with a mercury salt, the mercury ion must be complexed with sodium thiosulfate prior to distillation.

5. Apparatus

5.1 An all-glass distilling apparatus with an 800-1000 ml flask.

5.2 Spectrophotometer or filter photometer for use at 425 mμ and providing a light path of 1 cm or more.

5.3 Nessler tubes: Matched Nessler tubes (APHA Standard) about 300 mm long, 17 mm inside diameter, and marked at 225 mm ± 1.5 mm inside measurement from bottom.

5.4 Erlenmeyer flasks: The distillate is collected in 500 ml glass-stoppered flasks. These flasks should be marked at the 350 and the 500 ml volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks.

6. Reagents

6.1 Distilled water should be free of ammonia. Such water is best prepared by passage through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.

6.2 Ammonium chloride, stock solution, (1.0 ml = 1.00 mg NH_3-N). Dissolve 3.819 g NH_4Cl in water and bring to volume in a 1 liter volumetric flask for use as a stock solution.

6.3 Ammonium chloride, standard solution, (1.0 ml = 0.01 mg). Dilute 10 ml of this stock solution to 1 liter in a volumetric flask for use as the standard ammonium chloride solution.

6.4 Boric acid solution (20 g/1). - Dissolve 20 g H_3BO_3 in water and dilute to 1 liter.

6.5 Mixed indicator. - Mix 2 volumes of 0.2 percent methyl red in 95 percent ethyl alcohol with 1 volume of 0.2 percent methylene blue in 95 percent ethyl alcohol. This solution should be prepared fresh every 30 days.

Note 1 - Specially denatured ethyl alcohol conforming to Formula 3A or 30 of the U.S. Bureau of Internal Revenue may be substituted for 95 percent ethanol.

6.6 Nessler reagent. - Dissolve 100 g of mercuric iodide and. 70 g of potassium iodide in a small amount of water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 ml of water. Dilute the mixture to 1 liter. If this reagent is stored in a Pyrex bottle out of direct sunlight, it will remain stable for a period of up to 1 year.

Note 2 - This reagent should give the characteristic color with ammonia within 10 minutes after addition, and should not produce a precipitate with small amounts of ammonia (0.04 mg in a 50 ml volume).

6.7 Borate buffer. - Add 88 ml of 0.1 N NaOH solution to 500 ml of 0.025 M sodium tetraborate solution (5.0 g $Na_2B_4O_7$ per liter) and dilute to 1 liter.

6.8 Sulfuric acid, standard solution, (0.02 N, 1 ml = 0.28 mg NH_3-N). Prepare a stock solution of approximately 0.1 N acid by diluting 3 ml of concentrated H_2SO_4 (sp. gr. 1.84) to 1 liter with CO_2-free distilled water. Dilute 200 ml of this solution to 1 liter with CO_2-free distilled water. Standardize the approximately 0.02 N acid so prepared against 0.0200 N Na_2CO_3 solution. This last solution is prepared by dissolving 1.060 g anhydrous Na_2CO_3, oven-dried at 140°C, and diluting to 1 liter with CO_2-free distilled water.

Note 3 - An alternate and perhaps preferable method is to standardize the approximately 0.1 N H_2SO_4 solution against a 0.100 N Na_2CO_3 solution. By proper dilution the 0.0200 N acid can then be prepared.

6.9 Sodium hydroxide, 1 N. Dissolve 40 g NaOH in ammonia-free water and dilute to 1 liter.

6.10 Dechlorinating reagents. A number of dechlorinating reagents may be used to remove residual chlorine prior to distillation. These include:

(a) Sodium thiosulfate (1/70 N): Dissolve 3.5 g $Na_2S_2O_3$ in ammonia-free water and dilute to 1 liter. One ml of this solution will remove 1 mg/l of residual chlorine in 500 ml of sample.

(b) Sodium arsenite (1/70 N): Dissolve 1.0 g $NaAsO_2$ in ammonia-free water and dilute to 1 liter.

7. Procedure

7.1 Preparation of equipment. - Add 500 ml of ammonia-free water to an 800 ml Kjeldahl flask. The addition of boiling chips which have been previously treated with dilute NaOH will prevent bumping. Steam out the distillation apparatus until the distillate shows no trace of ammonia with Nessler reagent.

7.2 Sample preparation. - To 400 ml of sample add 1 N NaOH until the pH is 9.5, checking the pH during addition with a pH meter or by use of a short range pH paper.

7.3 Distillation. - Transfer the sample, the pH of which has been adjusted to 9.5, to an 800 ml Kjeldahl flask and add 25 ml of the borate buffer. Distill 300 ml at the rate of 6-10 ml/min. into 50 ml of 2% boric acid contained in a 500 ml glass stoppered Erlenmeyer flask. Dilute the distillate to 500 ml in the flask and nesslerize an aliquot to obtain an approximate value of the ammonia-nitrogen concentration. For concentrations above 1.0 mg/l the ammonia should be determined titrimetrically. For concentrations below this value it is determined colorimetrically.

7.4 Determination of ammonia in distillate. - Determine the ammonia content of the distillate either titrimetrically or colorimetrically as described below. (See 7.4.1 and 7.4.2).

7.4.1 Titrimetric determination. Add 3 drops of the mixed indicator to the distillate and titrate the ammonia with the 0.02 N H_2SO_4, matching the end point against a blank containing the same volume of ammonia-free water and H_3BO_3 solution.

7.4.2 Colorimetric determination. Prepare a series of Nessler tube standards as follows:

ml of Standard 1.0 ml = 0.01 mg NH_3/N	Conc., When Diluted to 50.0 ml, mg NH_3/N/liter
0.0 (Blank)	0.0
0.2	0.04
0.5	0.10
1.0	0.20
1.5	0.30
2.0	0.40
3.0	0.60
4.0	0.80

Dilute each tube to 50 ml with ammonia-free water, add 1.0 ml of Nessler reagent and mix. After 20 minutes read the optical densities at 425 mμ against the blank. From the values obtained plot optical density (absorbance) vs concentration for the standard curve.

7.4.3 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least 2 standards (a high and low) be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If distilled standards do not agree with undistilled standards the operator should find the cause of the apparent error before proceeding.

7.5 Determine the ammonia in the distillate by nesslerizing 50 ml or an aliquot diluted to 50 ml and reading the optical density at 425 mμ as described above for the standards. Ammonia-nitrogen content is read from the standard curve.

8. Calculations

8.1 Titrimetric

$$\text{mg/l } NH_3\text{-N} = \frac{A \times 0.28 \times 1000}{S}$$

in which:

A = ml 0.02 N H_2SO_4 used

S = ml sample

8.2 Spectrophotometric

$$\text{mg/l } NH_3\text{-N} = \frac{A \times 1000}{0.8\ S}$$

in which:

A = mg NH_3-N read from standard curve

S = volume of distillate nesslerized

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

NITROGEN, AMMONIA
(Automated Method)

1. Scope and Application

1.1 This method pertains to the determination of ammonia present in surface and saline waters. Depending upon the selection of the size of flow cell, and extent of dilution, concentrations in the range between .01 and 20 mg/liter N present as NH_3 may be determined.

2. Summary of Method

2.1 The intensity of the indophenol blue color(1), formed by the reaction of ammonia with alkaline phenol hypochlorite, is measured. Sodium nitroprusside is used to intensify the blue color.

3. Sample Handling and Preservation

3.1 Preservation by addition of 40 mg $HgCl_2$ per liter and refrigeration at 4°C.

4. Interferences

4.1 In sea water, calcium and magnesium ions are present in concentrations sufficient to cause precipitation problems during the analysis. This problem is eliminated by using 5% EDTA.

4.2 Any marked variation in acidity or alkalinity among samples should be eliminated, since the intensity of the color used to quantify the concentration is pH dependent. Likewise, the

Preceding page blank

pH of the wash water and the standard ammonia solutions should approximate that of the samples. For example, if the samples have been preserved with 1 ml concentrated H_2SO_4/liter, the wash water and standards should also contain 1 ml conc. H_2SO_4/l.

5. Apparatus

5.1 Technicon AutoAnalyzer Unit consisting of:

5.1.1 Sampler.

5.1.2 Manifold.

5.1.3 Proportioning pump.

5.1.4 Heating bath with double delay coil.

5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 630 or 650 mμ filters.

5.1.6 Recorder.

6. Reagents

6.1 Distilled Water: Special precaution must be taken to insure that distilled water is free of ammonia. Such water is prepared by passage of distilled water through an ion exchange column comprised of a mixture of both strongly acidic cation and strongly basic anion exchange resins. Since organic contamination may interfere with this analysis, use of the resin Dowex XE-75 or equivalent which also tends to remove organic impurities is advised. The regeneration of the ion exchange column should be carried out according to the instruction of the manufacturer.

6.2 Segmenting Fluid: Air scrubbed with 5N H_2SO_4. Ammonia free concentrated sulfuric acid and ammonia free distilled water used in the acid preparation.

6.3 Sodium Phenolate: Using a 1 liter Erlenmeyer flask, dissolve 83 g phenol in 500 ml distilled water. In small increments, cautiously add with agitation, 32 g of NaOH. Periodically, cool flask under water faucet. When cool, dilute to 1 liter.

6.4 Sodium Hypochlorite Solution ("Chlorox"): Dilute 100 ml of 5% "Chlorox" to 500 ml with distilled water. Available chlorine level should approximate 1%. Since "Chlorox" is a proprietary product and its formulation is subject to change, the analyst must remain alert to detecting any variation in this product significant to its use in this procedure.

6.5 EDTA (5%): Dissolve 50 g of EDTA (disodiumsalt) and approximately six pellets of NaOH in 1 liter of ammonia-free water.

6.6 Sodium Nitroprusside (0.005%): Dissolve 0.05 g of sodium nitroprusside in 1 liter of ammonia-free water.

6.7 Stock Solution: Dissolve 3.819 g of anhydrous ammonium chloride, NH_4Cl, dried at 105°C, in ammonia-free water, and dilute to 1 liter. 1 ml = 1.0 mg NH_3-N.

6.8 Standard Solution A: Dilute 10.0 ml of stock solution to 1 liter with ammonia-free water. 1 ml - .01 mg NH_3-N.

6.9 Standard Solution B: Dilute 10.0 ml of standard solution A to 100 ml with ammonia-free water. 1 ml = .001 mg NH_3-N.

6.10 Using standard solutions A and B, prepare the following standards in 100 ml volumetric flasks (prepare fresh each week):

NH_3-N, mg/l	ml Standard Solution/100 ml
	Solution B
0.01	1.0
0.02	2.0
0.05	5.0
0.10	10.0
	Solution A
0.20	2.0
0.50	5.0
0.80	8.0
1.00	10.0
1.50	15.0
2.00	20.0

Note: When saline water samples are analyzed, Substitute Ocean Water (SOW) should be used for preparing the above standards used for the calibration curve; otherwise, distilled water is used. If SOW is used, determine its blank background.

Substitute Ocean Water (SOW)

	g./l.		g./l.
NaCl	24.53	$NaHCO_3$	0.20
$MgCl_2$	5.20	KBr	0.10
Na_2SO_4	4.09	H_3BO_3	0.03
$CaCl_2$	1.16	$SrCl_2$	.03
KCl	0.70	NaF	.003

7. Procedure

7.1 For a working range of 0.01 to 2.00 NH_3-N mg/1, set up the manifold as shown in Figure 1. Higher concentrations may be accommodated by decreasing sample size and/or through dilution of sample.

7.2 Allow both colorimeter (with 650 mμ filters and 15 mm flow cell) and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding ammonia-free water through sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.3 Place a distilled water wash tube in alternate openings in sampler and set sample timing at 2.0 minutes. All tubes must be rinsed with ammonia-free water before use.

7.4 Arrange ammonia standards in sampler in order of decreasing concentration of nitrogen. Complete loading of sampler tray with unknown samples.

7.5 Switch sample line from distilled water to sampler and begin analysis.

8. Calculations

8.1 Prepare appropriate standard curve derived from processing ammonia standards through manifold. Compute concentration of samples by comparing sample peak heights with standard curve.

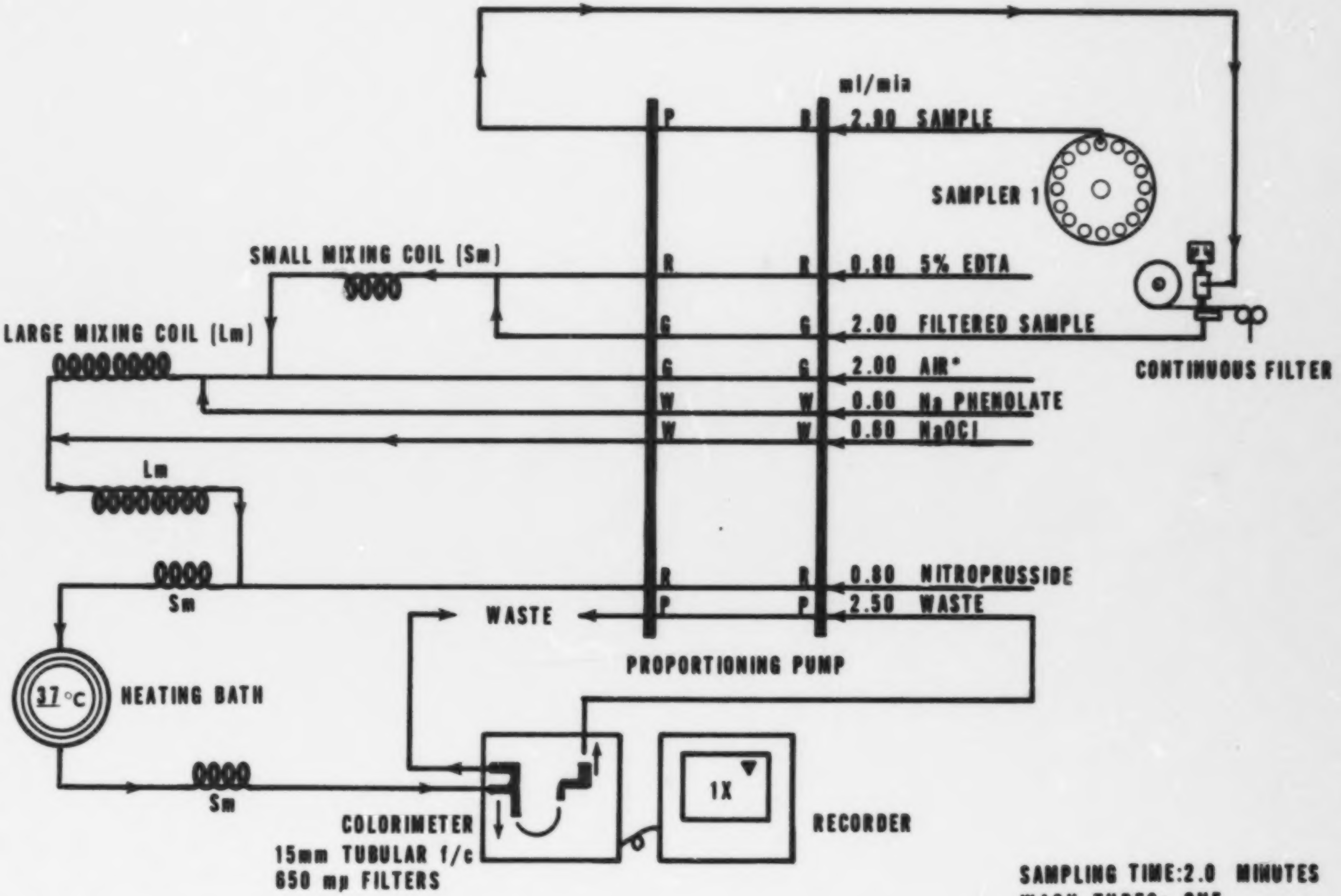
9. Precision and Accuracy

9.1 In a single laboratory (AQC), using surface water samples at concentrations of 1.41, 0.77, 0.59, and 0.43 mg NH_3-N/1, the standard deviation was ±0.005.

9.2 In a single laboratory (AQC), using surface water samples at concentrations of 0.16 and 1.44 mg NH_3-N/1, recoveries were 107% and 99%, respectively.

References

1. D. Van Slyke and A. Hiller, "Determination of Ammonia in Blood," J. Biol. Chem. 102, 499 (1933).
2. B. O'Connor, R. Dobbs, B. Villiers, and R. Dean, "Laboratory Distillation of Municipal Waste Effluents," JWPCP 39, R 25 (1967).
3. J. E. O'Brien and J. Fiore, "Ammonia Determination by Automatic Analysis," Wastes Engineering 33, 352 (1962).
4. A wetting agent recommended and supplied by the Technicon Corporation for use in Autoanalyzers.
5. ASTM "Manual on Industrial Water and Industrial Waste Water," 2nd Ed., 1966 printing, 418.


ml/min
P
R
2.00 SAMPLE
SAMPLER 1
SMALL MIXING COIL (Sm)
R
R
0.80 5% EDTA
LARGE MIXING COIL (Lm)
G
G
2.00 FILTERED SAMPLE
G
G
2.00 AIR*
CONTINUOUS FILTER
W
W
0.60 Na PHENOLATE
W
W
0.60 NaOCl
Lm
R
R
0.80 NITROPRUSSIDE
Sm
WASTE
P
P
2.50 WASTE
PROPORTIONING PUMP
37 °C
HEATING BATH
Sm
1X
COLORIMETER
15mm TUBULAR f/c
650 mμ FILTERS
RECORDER

SAMPLING TIME:2.0 MINUTES
WASH TUBES: ONE

*SCRUBBED THROUGH 5NH_2 SO_4

FIGURE 1. AMMONIA MANIFOLD

NITROGEN KJELDAHL, TOTAL

1. Scope and Application

1.1 This method covers the determination of total Kjeldahl nitrogen in surface waters, domestic and industrial wastes, and saline waters. The procedure converts nitrogen of components of biological origin such as amino acids, proteins and peptides to ammonia, but may not convert the nitrogenous compounds of some industrial wastes such as amines, nitro compounds, hydrazones, oximes, semi-carbazones and some refractory tertiary amines.

1.2 Two alternatives are listed for the determination of ammonia after distillation; the titrimetric method which is applicable to concentrations above 1 mg N/liter and the Nesslerization method which is applicable to concentrations below 1 mg N/liter.

1.3 This method is described for a macro system of glassware; however, micro glassware which does not change the chemistry of the procedure is equally applicable.

2. Definitions

2.1 Total Kjeldahl is defined as the sum of free ammonia and organic nitrogen compounds which are converted to ammonium sulfate $(NH_4)_2SO_4$, under the conditions of digestion described below.

2.2 Organic Kjeldahl Nitrogen is defined as the difference obtained by subtracting the free ammonia value (cf Nitrogen, Ammonia, this Manual) from the total Kjeldahl nitrogen value.

Proceding page blank

This may be determined directly by removal of ammonia before digestion.

3. Summary of Method

3.1 The sample is heated in the presence of concentrated sulfuric acid, K_2SO_4 and $HgSO_4$ and evaporated until SO_3 fumes are obtained and the solution becomes colorless or pale yellow. The residue is cooled, diluted, and is treated and made alkaline with a hydroxide-thiosulfate solution. The ammonia is distilled and determined after distillation either by nesslerization or titrimetrically.

4. Sample Handling and Preservation

4.1 Samples may be preserved by addition of 40 mg $HgCl_2$ and stored at 4°C. Even when so preserved, conversion of organic nitrogen to ammonia may occur. Preserved samples should be analyzed as soon as possible.

5. Apparatus

5.1 Digestion apparatus. A Kjeldahl digestion apparatus with 800 ml flasks and suction takeoff to remove SO_3 fumes and water is required. Use of micro-Kjeldahl equipment is also permissible.

5.2 Distillation apparatus. The Kjeldahl flask is connected to a condenser and an adaptor so that the distillate can be collected for nesslerization or in indicating H_3BO_3 solution for titration.

5.3 Spectrophotometer for use at 400 to 425 mμ with a light path of 1 cm or longer.

5.4 Nessler tubes, tall form, 50 ml.

6. Reagents

6.1 Distilled waters should be free of ammonia. Such water is best prepared by the passage of distilled water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.

6.2 Mercuric sulfate solution. Dissolve 8 g red, mercuric oxide (HgO) in 50 ml of 1:5 sulfuric acid and dilute to 100 ml with distilled water.

6.3 Sulfuric acid-mercuric sulfate-potassium sulfate solution. Dissolve 267 g K_2SO_4 in 1300 ml water and add 400 ml concentrated H_2SO_4. Add 50 ml mercuric sulfate solution and dilute to 2 liters.

6.4 Sodium hydroxide-sodium thiosulfate solution. Dissolve 500 g NaOH and 25 g $Na_2S_2O_3$ $5H_2O$ in water and dilute to 1 liter.

6.5 Phenolphthalein indicator solution. Dissolve 5 g phenolphthalein in 500 ml 95% ethyl alcohol or isopropanol and add 500 ml water. Add 0.02 NaOH dropwise until a faint, pink color appears.

6.6 Mixed indicator. Mix 2 volumes of 0.2% methyl red in 95% ethanol with 1 volume of 0.2% methylene blue in ethanol. Prepare fresh every 30 days.

6.7 Boric acid solution. Dissolve 20 g boric acid, H_2BO_3, in water and dilute to 1 liter with water.

6.8 Sulfuric acid titrant, 0.020 N. (1.00 ml = 0.28 mg N.)

6.9 Ammonium chloride, stock solution, (1.0 ml = 1.0 mg NH_3/N). Dissolve 3.819 g NH_4Cl in water and make up to 1.0 liter with ammonia free water.

6.10 Ammonium chloride, standard solution, (1.0 ml = 0.01 mg NH_3/N). Dilute 10.0 ml of the stock solution to 1.0 liter.

6.11 Nessler reagent. - Dissolve 100 g of mercuric iodide and 70 g of potassium iodide in a small volume of water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 ml of water. Dilute the mixture to 1 liter. The solution is stable for at least one year if stored in a pyrex bottle out of direct sunlight.

Note - Reagents 6.9, 6.10, and 6.11 are identical to reagents 6.2, 6.3 and 6.6 described under Nitrogen, Ammonia.

7. Procedure

7.1 The distillation apparatus should be pre-steamed before use by distilling a 1:1 mixture of ammonia-free water and sodium hydroxide-sodium thiosulfate solution until the distillate is ammonia free. This operation should be repeated each time the apparatus is out of service long enough to accumulate ammonia (usually 4 hours or more).

7.2 Place a measured sample or the residue from the distillation in the ammonia determination (for Organic Kjeldahl only) into an 800-ml Kjeldahl flask. The sample size can be determined from the following table:

Kjeldahl Nitrogen in Sample, mg/l	Sample Size ml
0 - 5	500
5 - 10	250
10 - 20	100
20 - 50	50.0
50 - 100	25.0

Dilute the sample, if required, to 500 ml, and add 100 ml sulfuric acid - mercuric sulfate - potassium sulfate solution (Note 2), and evaporate the mixture in the Kjeldahl apparatus until SO_3 fumes are given off and the solution turns colorless or pale yellow. Cool the residue and add 300 ml water.

Note 2 - Alternately digest the sample with 1 Kel-Pac (Olin-Matheson) and 20 ml H_2SO_4.

7.3 Make the digestate alkaline by careful addition of the sodium hydroxide-thiosulfate solution without mixing.

(Note - Slow addition of the heavy caustic solution down the tilted neck of the digestion flask will cause the heavier solution to underlay the aqueous sulfuric acid solution without loss of free ammonia. Do not mix until the digestion flask has been connected to the distillation apparatus.)

7.4 Connect the Kjeldahl flask to the condenser with the tip of condenser (or an extension of the condenser tip) below the level of the boric acid solution in the receiving flask.

7.5 Distill 300 ml at the rate of 6-10 ml/min., into 50 ml of 2% boric acid contained in a 500-ml glass stoppered Erlenmeyer flask.

7.5.1 If it is anticipated that the ammonia measurement will be by nesslerization, 50 ml of boric acid is preferred. If, however, sufficient ammonia is present to permit titration of a larger volume of boric acid, either 100 or 200 ml, may be used.

7.6 Dilute the distillate to 500 ml in the flask and nesslerize an aliquot, to obtain an approximate value of the ammonia-nitrogen concentration. For concentrations above 1.0 mg/l the ammonia should be determined titrimetrically. For concentrations below this value it is determined colorimetrically.

7.7 Determination of ammonia in distillate. - Determine the ammonia content of the distillate either titrimetrically or colorimetrically as described below.

7.7.1 Titrimetric determination. Add 3 drops of the mixed indicator to the distillate and titrate the ammonia with the 0.02 N H_2SO_4, matching the endpoint against a blank containing the same volume of ammonia-free water and H_3BO_3 solution.

7.7.2 Colorimetric determination. Prepare a series of Nessler tube standards as follows:

ml of Standard 1.0 ml = 0.01 mg NH_3/N	Conc., When Diluted to 50.0 ml, mg NH_3/N/liter
0.0 (Blank)	0.0
0.2	0.04
0.5	0.10
1.0	0.20
1.5	0.30
2.0	0.40
3.0	0.60
4.0	0.80

Dilute each tube to 50 ml with ammonia-free water, add 1.0 ml of Nessler reagent and mix. After 20 minutes read the optical densities at 425 mμ against the blank. From the values obtained plot optical density (absorbance) vs concentration for the standard curve.

7.7.3 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least 2 standards (a high and low) be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If distilled standards do not agree with undistilled standards the operator should find the cause of the apparent error before proceeding.

7.8 Determine the ammonia in the distillate by nesslerizing 50 ml or an aliquot diluted to 50 ml and reading the optical density at 425 mμ as described above for the Standards. Ammonia-nitrogen is read from the standard curve.

8. Calculation

8.1 If the titrimetric procedure is used calculate Total Kjeldahl Nitrogen, in mg/l, in the original sample as follows:

$$\text{Total Kjeldahl nitrogen, mg/l} = \frac{(A-B) \times N \times F \times 1000}{S}$$

where:

A = milliliters of standard 0.020 N H_2SO_4 solution used in titrating sample.

B = milliliters of standard 0.020 N H_2SO_4 solution used in titrating blank.

N = normality of sulfuric acid solution.

F = millequivalent weight of nitrogen (14 mg).

S = milliliters of sample digested.

If the sulfuric acid is exactly 0.02 N the formula is shortened to:

$$\text{TKN, mg/l} = \frac{(A-B) \times 280}{S}$$

8.2 If the Nessler procedure is used, calculate the Total Kjeldahl Nitrogen, in mg/l, in the original sample as follows:

$$\text{TKN, mg/l} = \frac{A \times 1000}{0.8 \times S}$$

where:

A = mg NH_3/N read from curve.

S = volume of distillate nesslerized.

8.3 Calculate Organic Kjeldahl Nitrogen in mg/l, as follows:

$$\text{Organic Kjeldahl Nitrogen} = \text{TKN} - NH_3/N$$

9. Precision

9.1 Precision and accuracy data are not available at this time.

NITROGEN, KJELDAHL, TOTAL

(Automated Phenolate Method)

1. Scope and Application

1.1 This automated method may be used to determine Kjeldahl nitrogen in surface waters, domestic and industrial wastes, and saline waters. The applicable range is 0.05 to 2.0 mg N/l. Approximately 20 samples per hour can be analyzed.

2. Summary of Method

2.1 The sample is automatically digested with a sulfuric acid solution containing potassium sulfate and mercuric sulfate as a catalyst to convert organic nitrogen to ammonium sulfate. The solution is then automatically neutralized with sodium hydroxide solution and treated with alkaline phenol reagent and sodium hypochlorite reagent. This treatment forms a blue color designated as indophenol. Sodium nitroprusside, which increases the intensity of the color, is added to obtain necessary sensitivity for measurement of low level nitrogen.(1)

3. Definitions

3.1 Total Kjeldahl nitrogen is defined as the sum of free ammonia and of organic compounds which are converted to $(NH_4)_2SO_4$ under the conditions of digestion which are specified below.

3.2 Organic Kjeldahl nitrogen is defined as the difference obtained by subtracting the free ammonia value from the total Kjeldahl nitrogen value. Also, organic Kjeldahl nitrogen may be determined directly by removal of ammonia before digestion.

4. Sample Handling and Preservation

4.1 Preservation by addition of 40 mg $HgCl_2$ per liter and refrigeration at 4°C is necessary.

5. Interferences

5.1 Iron and chromium ions tend to catalyze while copper ions tend to inhibit the indophenol color reaction.

6. Apparatus

6.1 Technicon AutoAnalyzer consisting of:

6.1.1 Sampler II, equipped with continuous mixer.

6.1.2 Two proportioning pumps.

6.1.3 Manifold I

6.1.4 Manifold II

6.1.5 Continuous Digester

6.1.6 Peristaltic pump

6.1.7 Five-gallon Carboy fume-trap

6.1.8 80°C Heating bath

6.1.9 Colorimeter equipped with 50 mm tubular flow cell and 630 mμ filters.

6.1.10 Recorder equipped with range expander.

7. Reagents

7.1 Distilled Water: Special precaution must be taken to insure that distilled water is free of ammonia. Such water is prepared by passage of distilled water through an ion exchange column comprised of a mixture of both strongly acidic cation and strongly basic anion exchange resins. Furthermore, since organic contamination may interfere with this analysis, use of the resin Dowex XE-75 or equivalent which also tends to remove organic impurities is advised. The regeneration of the ion exchange column should be carried out according to the instruction of the manufacturer.

7.2 Sulfuric acid: As it readily absorbs ammonia, special precaution must also be taken with respect to its use. Do not store bottles reserved for this determination in areas of potential ammonia contamination.

7.3 EDTA (2% solution): Dissolve 20 g disodium ethylenediamine tetraacetate in 1 liter of distilled water. Adjust pH to 10.5-11.

7.4 Sodium hydroxide (30% solution): Dissolve 30 g NaOH in 1 liter of distilled water. (May have to be adjusted to give neutralization in the water-jacketed mixing coil).

7.5 Sodium nitroprusside, Stock (1% solution): Dissolve 10 g $Na_2Fe(CN)_5NO.2H_2O$ in 1 liter distilled H_2O.

7.6 Sodium nitroprusside, working solution: Dilute 50 ml stock solution to 1 liter with distilled water.

7.7 Alkaline phenol reagent: Pour 550 mls liquid phenol (88-90%) slowly with mixing and cooling into 1 liter of 40% NaOH. Make up to 2 liters with distilled water.

7.8 Sodium hypochlorite (1% solution): Dilute commercial "Clorox" - 200 ml to 1 liter with distilled water.

7.9 Digestion mixture: Place 2 g HgO in a 2-liter container. Slowly add, with stirring, 300 ml of acid water (100 ml H_2SO - 200 ml H_2O) and stir until cool. Add 100 ml 10% K_2SO_4. Dilute to a volume of 2 liters with conc. sulfuric acid (approximately 500 ml at a time, allowing time for cooling).

7.10 Stock Solution: Dissolve 4.7619 g of pre-dried ammonium sulfate in distilled water and dilute to 1.0 liter. Dissolve 2.1276 g of urea in distilled water and dilute to 1.0 liter. Dissolve 10.5263 g of glutamic acid in distilled water and dilute to 1.0 liter. 1 ml = 1.0 mg N.

7.11 Standard Solution: Dilute 10.0 ml of respective stock solution to 1.0 liter. 1 ml = 0.01 mg N.

7.11.1 Using the respective standard solutions, prepare the following standards in 100.0-ml volumetric flasks:

Conc., mg N/1	ml Standard Solution/100 ml
0.00	0.0
0.05	0.5
0.10	1.0
0.20	2.0
0.40	4.0
0.60	6.0
0.80	8.0
1.00	10.0
1.50	15.0
2.00	20.0

8. Procedure

8.1 Set up manifolds as shown in Figures 1, 2, and 3.

8.1.1 In the operation of Manifold No. 1, the control of three key factors is required to enable Manifold No. 2 to receive the mandatory representative feed. First, the digestate flowing into the pulse chamber (PC-1) must be bubble free, otherwise, air will accumulate in A-7, thus altering the ratio of sample to digestate in digestor. Second, in maintaining even flow from the helix, the peristaltic pump must be adjusted to cope with differences in density of the digestate and the wash water. Third, the sample pick-up rate from the helix must be precisely adjusted to insure that the entire sample is aspirated into the mixing chamber. And finally, the contents of the "Mixing Chamber" must be kept homogeneous by the proper adjustment of the air bubbling rate.

8.1.2 In the operation of Manifold No. 2, it is important in the neutralization of the digested sample to adjust the concentration of the NaOH so that the waste from the C-3 debubbler is slightly acid to Hydrion B paper.

8.1.3 The digester temperature is 360°C for the first stage and 330°C for the second and third stages.

8.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

8.3 Set sampling rate of Sample II at 20 samples per hour, using a wash to sample ratio of 2 to 1.

8.4 Arrange various standards in Sampler cups in order of increasing concentration. Complete loading of sampler tray with unknown samples.

8.5 Switch sample line from distilled water to sampler and begin analysis.

8.5.1 If equipment is operating properly, 100% nitrogen recovery should be obtained for glutamic acid and urea when compared to ammonium sulfate standards.

9. Calculation

9.1 Prepare standard curve by plotting peak heights of processed standards against concentration values. Compute concentration of samples by comparing sample peak heights with standard curve.

9.2 Any sample that has a computed concentration that is less than 10% of the sample run immediately prior to it must be rerun.

10. Precision and Accuracy

10.1 Precision and accuracy data are not available at this time.

References

1. Kammerer, P.A.; Rodel, M.G.; Hughes, R.A.; and Lee, G.F.; "Low Level Kjeldahl Nitrogen Determination on the Technicon AutoAnalyzer." Environmental Science and Technology. 1:4:340 (April 1967).
2. McDaniel, William H.; Hemphill, R.N.; Donaldson, W.T.; "Automatic Determination of Total Kjeldahl Nitrogen in Estuarine Waters." Presented at Technicon Symposium on Automation in Analytical Chemistry, New York, October 3, 1967.
3. B. O'Connor, Dobbs, Villiers, and Dean, "Laboratory Distillation of Municipal Waste Effluents". JWPCP 39, R 25, 1967.

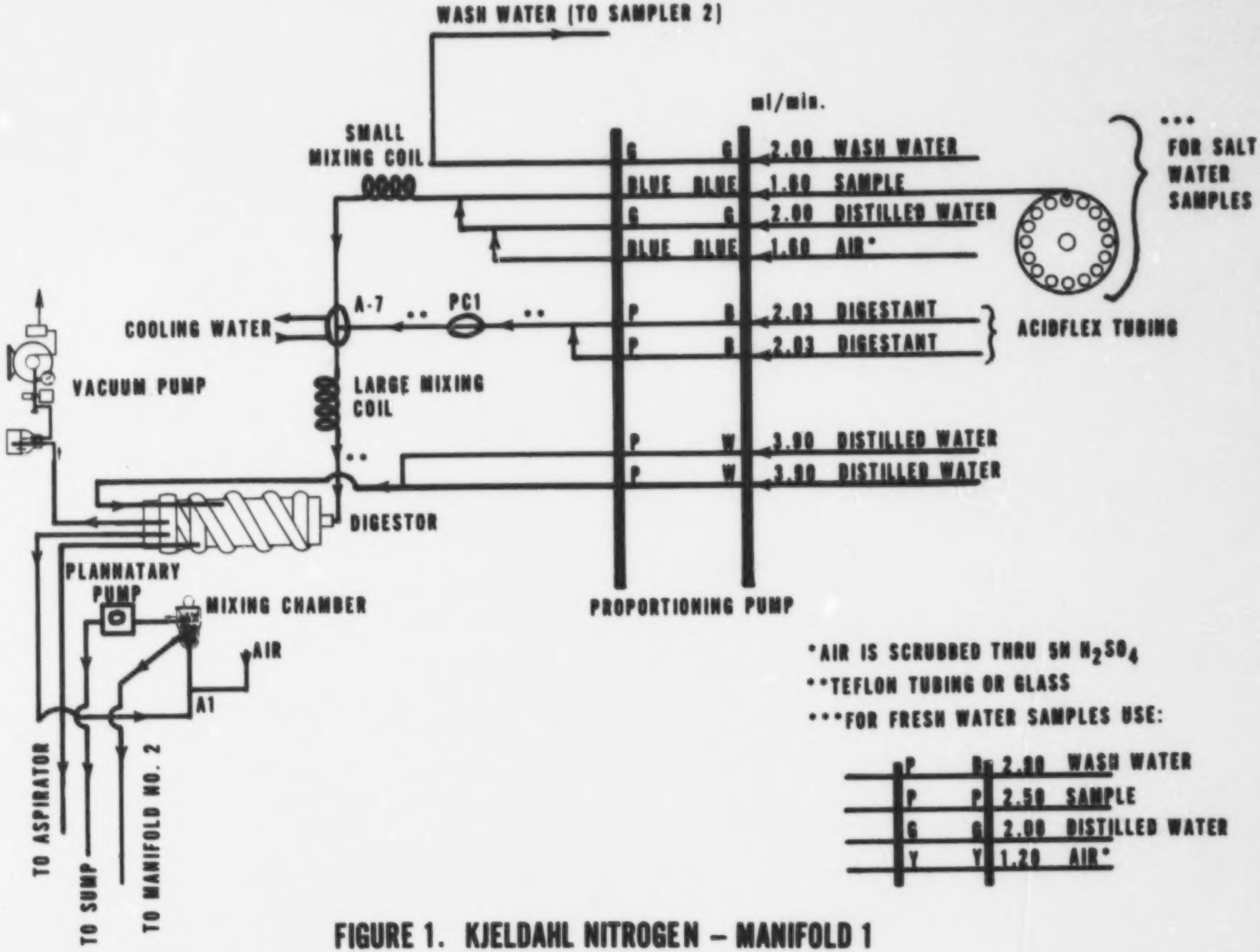

WASH WATER (TO SAMPLER 2)
ml/min.
SMALL MIXING COIL
G G 2.00 WASH WATER
BLUE BLUE 1.60 SAMPLE
G G 2.00 DISTILLED WATER
BLUE BLUE 1.60 AIR*
***
FOR SALT WATER SAMPLES
A-7
PC1
**
COOLING WATER
P B 2.03 DIGESTANT
P B 2.03 DIGESTANT
ACIDFLEX TUBING
VACUUM PUMP
LARGE MIXING COIL
P W 3.90 DISTILLED WATER
P W 3.90 DISTILLED WATER
DIGESTOR
PLANNATARY PUMP
MIXING CHAMBER
PROPORTIONING PUMP
AIR
A1
TO ASPIRATOR
TO SUMP
TO MANIFOLD NO. 2
*AIR IS SCRUBBED THRU 5N H_2SO_4
**TEFLON TUBING OR GLASS
***FOR FRESH WATER SAMPLES USE:
P B 2.90 WASH WATER
P P 2.50 SAMPLE
G G 2.00 DISTILLED WATER
Y Y 1.20 AIR*

FIGURE 1. KJELDAHL NITROGEN – MANIFOLD 1

CONTINUOUS DIGESTER & MIXING CHAMBER ASSEMBLY

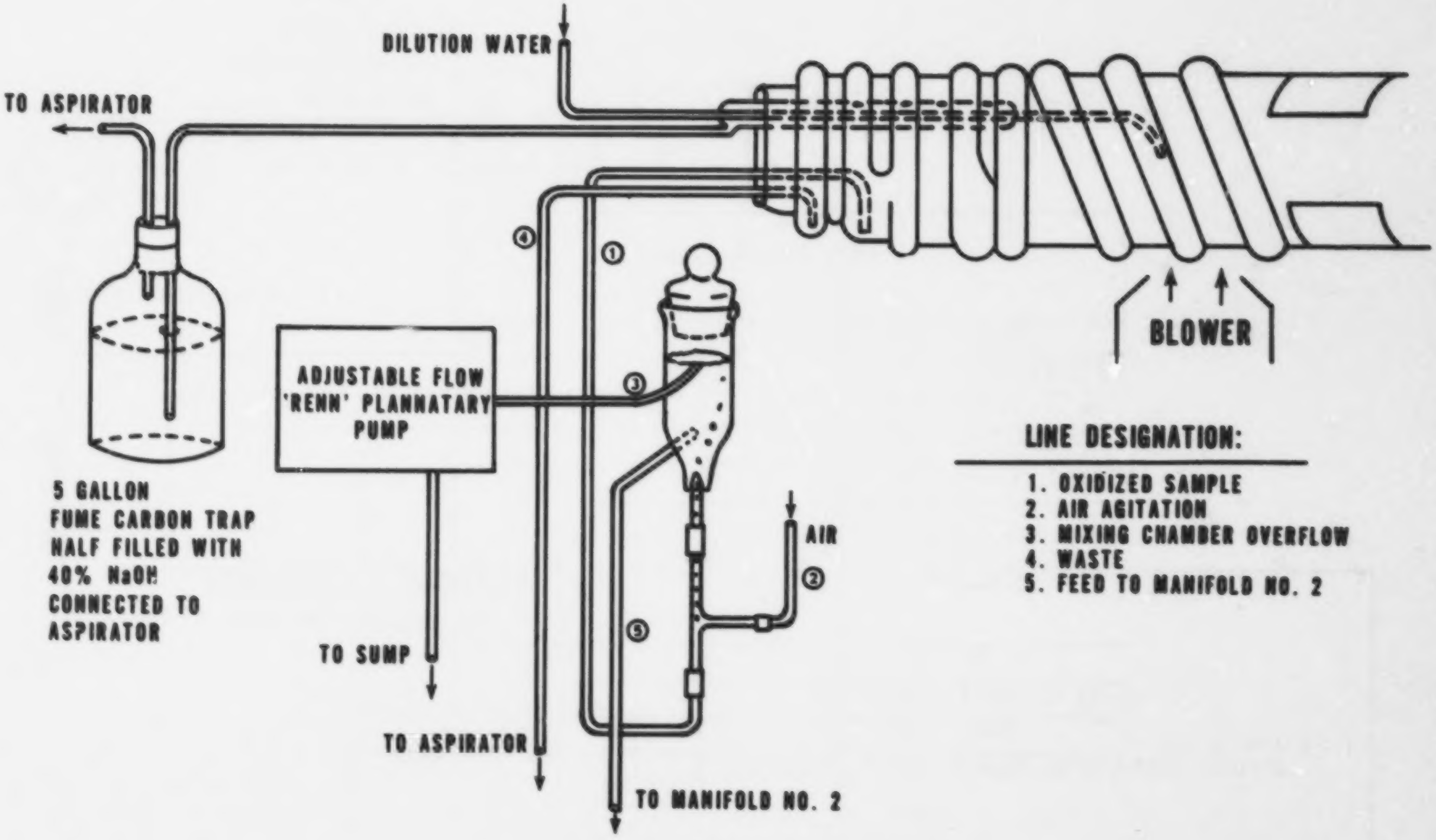

DILUTION WATER
TO ASPIRATOR
④
①
③
⑤
②
AIR
BLOWER
ADJUSTABLE FLOW 'RENN' PLANNATARY PUMP
5 GALLON FUME CARBON TRAP HALF FILLED WITH 40% NaOH CONNECTED TO ASPIRATOR
TO SUMP
TO ASPIRATOR
TO MANIFOLD NO. 2
LINE DESIGNATION:
1. OXIDIZED SAMPLE
2. AIR AGITATION
3. MIXING CHAMBER OVERFLOW
4. WASTE
5. FEED TO MANIFOLD NO. 2

FIGURE 2. KJELDAHL NITROGEN

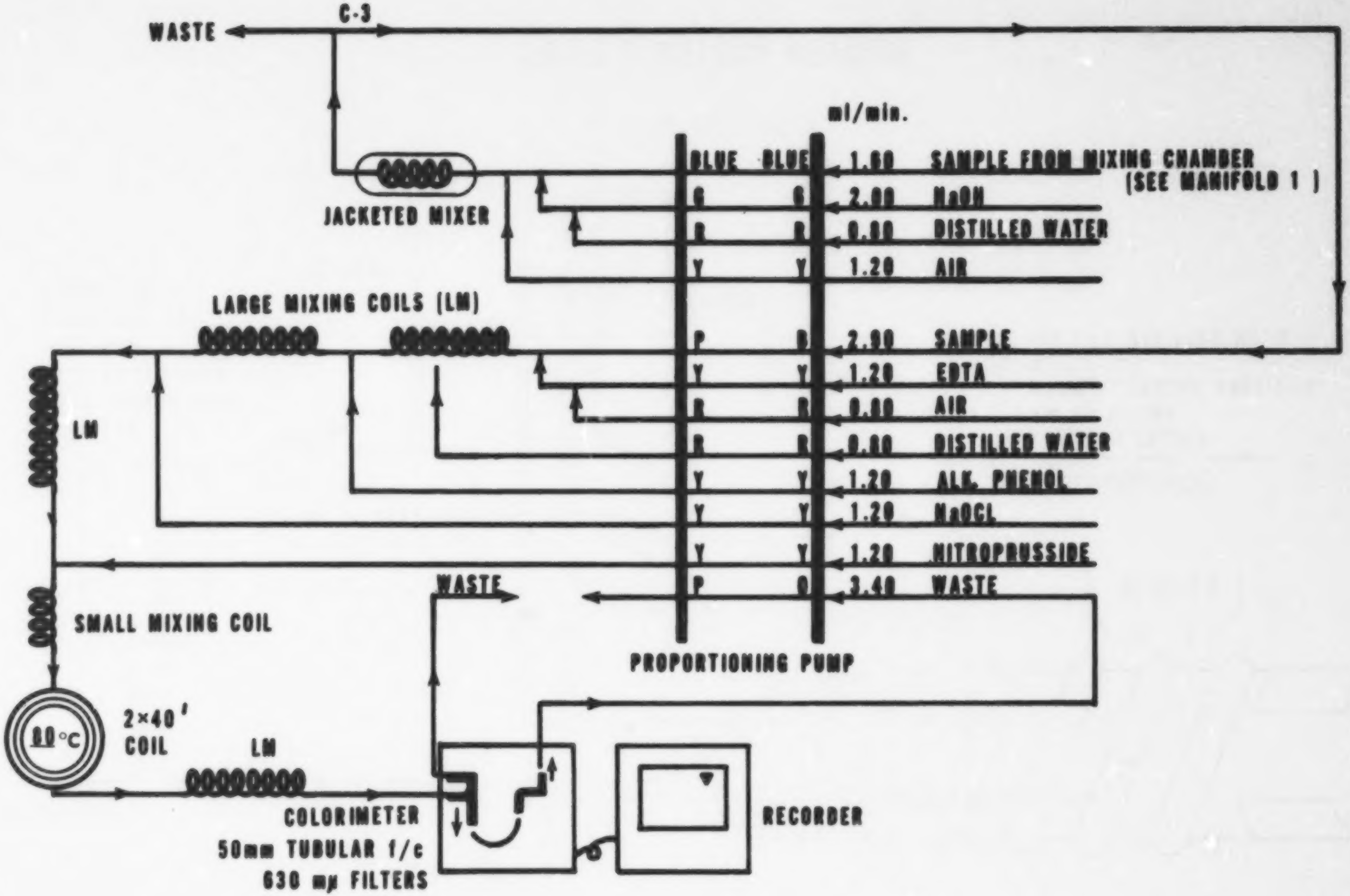

WASTE
C-3
ml/min.
JACKETED MIXER
BLUE BLUE 1.60 SAMPLE FROM MIXING CHAMBER (SEE MANIFOLD 1)
G G 2.00 NaOH
R R 0.80 DISTILLED WATER
Y Y 1.20 AIR
LARGE MIXING COILS (LM)
P B 2.90 SAMPLE
Y Y 1.20 EDTA
R R 0.80 AIR
R R 0.80 DISTILLED WATER
Y Y 1.20 ALK. PHENOL
Y Y 1.20 NaOCL
Y Y 1.20 NITROPRUSSIDE
P O 3.40 WASTE
LM
WASTE
SMALL MIXING COIL
PROPORTIONING PUMP
80°C
2×40' COIL
LM
COLORIMETER
50mm TUBULAR f/c
630 mμ FILTERS
RECORDER

FIGURE 3. KJELDAHL NITROGEN MANIFOLD 2.

NITROGEN, NITRATE

1. Scope and Application

1.1 This method is applicable to the analysis of surface waters, domestic and industrial wastes, and saline waters. Modification can be made to remove or correct for turbidity, color, salinity, or dissolved organic compounds in the sample.

1.2 The applicable range of concentrations is 0.1 to 2 mg NO_3-N/ liter.

2. Summary of Method

2.1 This method is based upon the reaction of the nitrate ion with brucine sulfate in a 13 N H_2SO_4 solution at a temperature of 100°C. The color of the resulting complex is measured at 410 mμ. Temperature control of the color reaction is extremely critical.

3. Sample Handling and Preservation

3.1 Until more conclusive data is obtained, samples may be preserved by addition of 40 mg $HgCl_2$ per liter and storage at 4°C.

4. Interferences

4.1 Dissolved organic matter will cause an off color in 13 N H_2SO_4 and must be compensated for by additions of all reagents. except the brucine-sulfanilic acid reagent. This also applies to natural color present not due to dissolved organics.

4.2 The effect of salinity is eliminated by addition of sodium chloride to the blanks, standards and samples.

4.3 All strong oxidizing or reducing agents interfere. The presence of oxidizing agents may be determined by the addition of orthotolidine reagent.

4.4 Residual chlorine interference is eliminated by the addition of sodium arsenite.

4.5 Ferrous and ferric iron and quadrivalent manganese give slight positive interference, but in concentrations less than 1 mg/l these are negligible.

4.6 Uneven heating of the samples and standards during the reaction time will result in erratic values. The necessity for absolute control of temperature during the critical color development period cannot be too strongly emphasized.

5. Apparatus

5.1 Spectrophotometer or filter photometer suitable for measuring optical densities at 410 mμ and capable of accommodating 25 mm diameter cells.

5.2 Sufficient number of 25 mm diameter matched tubes for reagent blanks, standards, and samples.

5.3 Neoprene coated wire racks to hold 25 mm diameter tubes.

5.4 Water bath suitable for use at 100°C. This bath should contain a stirring mechanism so that all tubes are at same temperature and should be of sufficient capacity to accept the required number of tubes without significant drop in temperature when the tubes are immersed.

5.5 Water bath suitable for use at 10-15°C.

6. Reagents

6.1 Distilled water free of nitrite and nitrate is to be used in preparation of all reagents and standards.

6.2 Sodium chloride solution (300 g/l). Dissolve 300 g NaCl in distilled water and dilute to 1000 ml.

6.3 Sulfuric acid solution. Carefully add 500 ml H_2SO_4 (sp. gr. 1.84) to 125 ml distilled water. Cool and keep tightly stoppered to prevent absorption of atmospheric moisture.

6.4 Brucine-sulfanilic acid reagent. Dissolve 1 g brucine sulfate $[(C_{23}H_{26}N_2O_4)_2 . H_2SO_4 . 7H_2O]$ and 0.1 g sulfanilic acid $(NH_2C_6H_4SO_3H . H_2O)$ in 70 ml hot distilled water. Add 3 ml concentrated HCl, cool, mix and dilute to 100 ml. Store in a dark bottle at 5°C. This solution is stable for several months; the pink color that develops slowly does not effect its usefulness. Mark bottle with warning: CAUTION: Brucine Sulfate is toxic; take care to avoid ingestion.

6.5 Potassium nitrate stock solution (1 ml = 0.1 mg NO_3-N). Dissolve 0.7218 g anhydrous potassium nitrate (KNO_3) in distilled water and dilute to 1 liter.

6.6 Potassium nitrate standard solution (1 ml = 0.01 mg NO_3-N). Dilute 100 ml of the stock solution to 1 liter. This standard solution should be prepared fresh weekly.

6.7 Acetic acid (1 + 3). Dilute 1 vol. glacial acetic acid (CH_3COOH) with 3 volumes of distilled water.

7. Procedure

7.1 Adjust the pH of the samples to approximately pH 7 with 1:3 acetic acid and, if necessary, filter through a 0.45 μ pore size filter.

7.2 Set up the required number of matched tubes in the rack to handle reagent blank, standards and samples. It is suggested that tubes be spaced evenly throughout the rack to allow for even flow of bath water between the tubes. Even spacing of tubes should assist in achieving uniform heating of all tubes.

7.3 If it is necessary to correct for color or dissolved organic matter which will cause color on heating, a set of duplicate tubes must be used to which all reagents except the brucine-sulfanilic acid has been added.

7.4 Pipette 10 ml or an aliquot of the samples diluted to 10 ml into the sample tubes.

7.5 If the samples are saline, add 2.0 ml of the 30 percent sodium chloride solution to the reagent blank, standards and samples. For fresh water samples, sodium chloride solution may be omitted. Mix contents of tubes of swirling and place rack in cold water bath (0-10°C).

7.6 Pipette 10 ml of sulfuric acid solution into each tube and mix by swirling. Allow tubes to come to thermal equilibrium in the cold bath. Be sure that temperatures have equilibrated in all tubes before continuing.

7.7 Add 0.5 ml brucine-sulfanilic acid reagent to each tube (except the interference control tubes) and carefully mix by swirling, then place the rack of tubes in the boiling water bath for exactly 25 minutes. CAUTION: Immersion of the tube rack into the bath should not decrease the temperature of the bath. Flow of bath water between the tubes should not be restricted by crowding too many tubes into the rack. If color development in the standards reveals discrepancies in theprocedure the operator should repeat the procedure after reviewing the temperature control steps.

7.8 Remove rack of tubes from the hot water bath and immerse in the cold water bath and allow to reach thermal equilibrium (20-25°C).

7.9 Dry tubes and read optical density against the reagent blank at 410 mμ.

8. Calculation

8.1 Obtain a standard curve by plotting the optical densities of standards run by the above procedure against mg NO_3-N. (The color reaction does not always follow Beer's law.)

8.2 Subtract the absorbance of the sample without the brucine-sulfanilic reagent from the absorbance of the sample containing brucine-sulfanilic acid and read the optical density in mg NO_3-N. Multiply by factor for converting mg per aliquot of sample to mg per liter.

$$NO_3\text{-N mg/l} = \text{mg } NO_3\text{-N from curve} \times \frac{1000}{\text{ml sample}}$$

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

NITROGEN, NITRATE AND NITRITE

(Automated Hydrazine Reduction Method)

1. Scope and Application

   1.1 This method is applicable to surface waters, and domestic and industrial wastes which contain less than 500 mg/l calcium. The applicable range of this method is 0.05-10 mg/l nitrite or nitrate nitrogen. Approximately 20 samples per hour can be analyzed.

2. Summary of Method

   2.1 This method, using the Technicon AutoAnalyzer, determines NO_2-N by the conventional diazotization-coupling reaction. The NO_3-N is reduced with hydrazine sulfate in another portion of the sample and the nitrite thus formed is determined in the usual manner.

   2.2 Subtraction of the NO_2-N originally present in the sample from the total NO_2-N found will give the original NO_3-N concentration in terms of NO_2-N.

3. Sample Handling and Preservation

   3.1 Preservation by addition of 40 mg $HgCl_2$ per liter and refrigeration at 4°C.

4. Interferences

   4.1 The following table lists the concentration of ions that cause no interference in the determination of nitrite and nitrate nitrogen. The same interfering ion concentration applies to either nitrite or nitrate:

Ion	mg/l Ion Not Causing Interference
Cl^-	30,000
PO_4^{-3}	50
S^{-2}	Note
NH_3-N	80
Mg^{+2}	75
Ca^{+2}	240
Fe^{+3}	30
ABS	60

Note 1. -- The apparent NO_3 and NO_2 concentrations varied ± 10 percent with concentrations of sulfide ion up to 10 mg/l.

4.2 The pH of the samples should be between 6 and 9.

5. Apparatus

5.1 Technicon AutoAnalyzer consisting of:

5.1.1 Two proportional pumps.

5.1.2 Two colorimeters each with an 8 mm flow-through cell and 520 mμ filters.

5.1.3 One continuous filter.

5.1.4 One Sampler I.

5.1.5 Two recorders.

5.1.6 One 38°C temperature bath.

5.1.7 Two time delay coils.

6. Reagents

6.1 Color developing reagent: To approximately 3 liters of distilled water add 400 ml concentrated phosphoric acid (sp. gr. 1.834), 60 g sulfanilamide ($H_2N-C_6H_4\ SO_2\ NH_2$) followed by 3.0 g N (1-Naphthyl)ethylene-diamine dihydrochloride. Dilute the solution to 4 liters with distilled water and store in a dark bottle in the refrigerator. This solution is stable for approximately 1 month.

Note 2 -- It may be necessary to apply heat in order to dissolve the sulfanilamide.

6.2 Copper sulfate; stock solution: Dissolve 2.5 g of copper sulfate ($CuSO_4.5H_2O$) in distilled water and dilute to 1 liter.

6.3 Copper sulfate; dilute solution: Dilute 20 ml of stock solution to 2 liters with distilled water.

6.4 Sodium hydroxide; stock solution, (10 N): Dissolve 400 g NaOH in 750 ml distilled water, cool and dilute to 1 liter.

6.5 Sodium hydroxide(1.0N): Dilute 100 ml of stock NaOH solution to 1 liter.

6.6 Sodium hydroxide(0.3N): Dilute 60 ml of stock NaOH to 2 liters.

6.7 Hydrazine sulfate solution: Dissolve 54.92 g of hydrazine sulfate ($N_2H_4.H_2SO_4$) in 1800 ml of distilled water and dilute to 2000 ml. This solution is stable for approximately 6 months.

CAUTION: Toxic if ingested. Mark container with warning.

6.8 Potassium nitrate; stock solution (1000 mg/l . NO_3-N): Dissolve 7.2180 g of KNO_3, oven dried at 100-105°C for 2 hours, in distilled water and dilute to 1000 ml. Add 1 ml chloroform as a preservative. Stable for 6 months.

6.9 Potassium nitrate; standard solution (100 mg/l NO_3-N): Dilute 50 ml of stock KNO_3 solution to 500 ml in a volumetric flask. From this dilute solution prepare the following standards in 500 ml volumetric flasks:

mg/l NO_3-N	ml Standard Solution
0.4	2.0
1.0	5.0
1.6	8.0
3.0	15.0
5.0	25.0
7.0	35.0
10.0	50.0

6.10 Potassium nitrite; stock solution (1000 mg/l NO_2-N): Dissolve 4.9260 g $NaNO_2$, oven dried at 100-105°C for two hours, in distilled water and dilute to 1000 ml. Add 1 ml chloroform as preservative. Store in the refrigerator. Stable for 1 month.

6.11 Potassium nitrite; standard solution (100 mg/l): Dilute 50 ml of stock $NaNO_2$ solution to 500 ml in a volumetric flask. From this dilute solution prepare the same volumetric standards as in 6.9. Prepare fresh each week.

7. Procedure

7.1 Set up the manifold as shown in Figures 1 and 2. Allow both colorimeter (with the proper filters) and recorder to warm up for 30 minutes, then run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on each colorimeter. Adjust baseline to 0.01 optical density. Place a distilled water wash tube in alternate openings on sampler and set sample timing at 1.5 minutes.

7.2 Run a 2.0 mg/l NO_3-N and a 2.0 mg/l NO_2-N standard through the system to check for 100% reduction of nitrate to nitrite. The two peaks should be of equal height. If the NO_3 peak is lower than that of the NO_2 peak, the temperature of the reduction bath should be increased until they are equal. If the NO_3 peak is higher than the nitrate, the temperature should be reduced. When the correct temperature of the bath has been determined, no further adjustment should be necessary.

7.3 Arrange standards in sampler in NO_2-NO_3 order with increasing concentration of nitrogen. Place unknown samples in sampler tubes and place in alternate openings of sampler. A NO_2 and NO_3 standard of equal nitrogen concentration should be placed after every 10 samples as a further check on the system and to more easily identify peaks.

8. Calculation

   8.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentrations of samples by comparing sample peak heights with standard curve.

   8.2 Subtract the NO_2 concentration in the sample from the total NO_2 found (nitrite plus nitrate) on the reduction side to calculate the NO_3 concentration in the sample.

9. Precision and Accuracy

   9.1 In a single laboratory (AQC), using surface water samples at concentrations of 0.1, 0.2, 0.8, and 2.1 mg-N/$_1$, the standard deviations were 0.0, ±0.04, ±0.05, and ±0.05, respectively.

   9.2 In a single laboratory (AQC), using surface water samples at concentrations of 0.2 and 2.2 mg-N/$_1$, recoveries were 100% and 96%, respectively.

References

1. D. Jenkins and L. Medsker, "Brucine Method for Determination of Nitrate in Ocean, Estuarine, and Fresh Waters." Anal. Chem., 36, 610 (1964).

2. L. Kamphake, S. Hannah, and J. Cohen, "Automated Analysis for Nitrate by Hydrazine Reduction." Water Research, 1, 205 (1967).

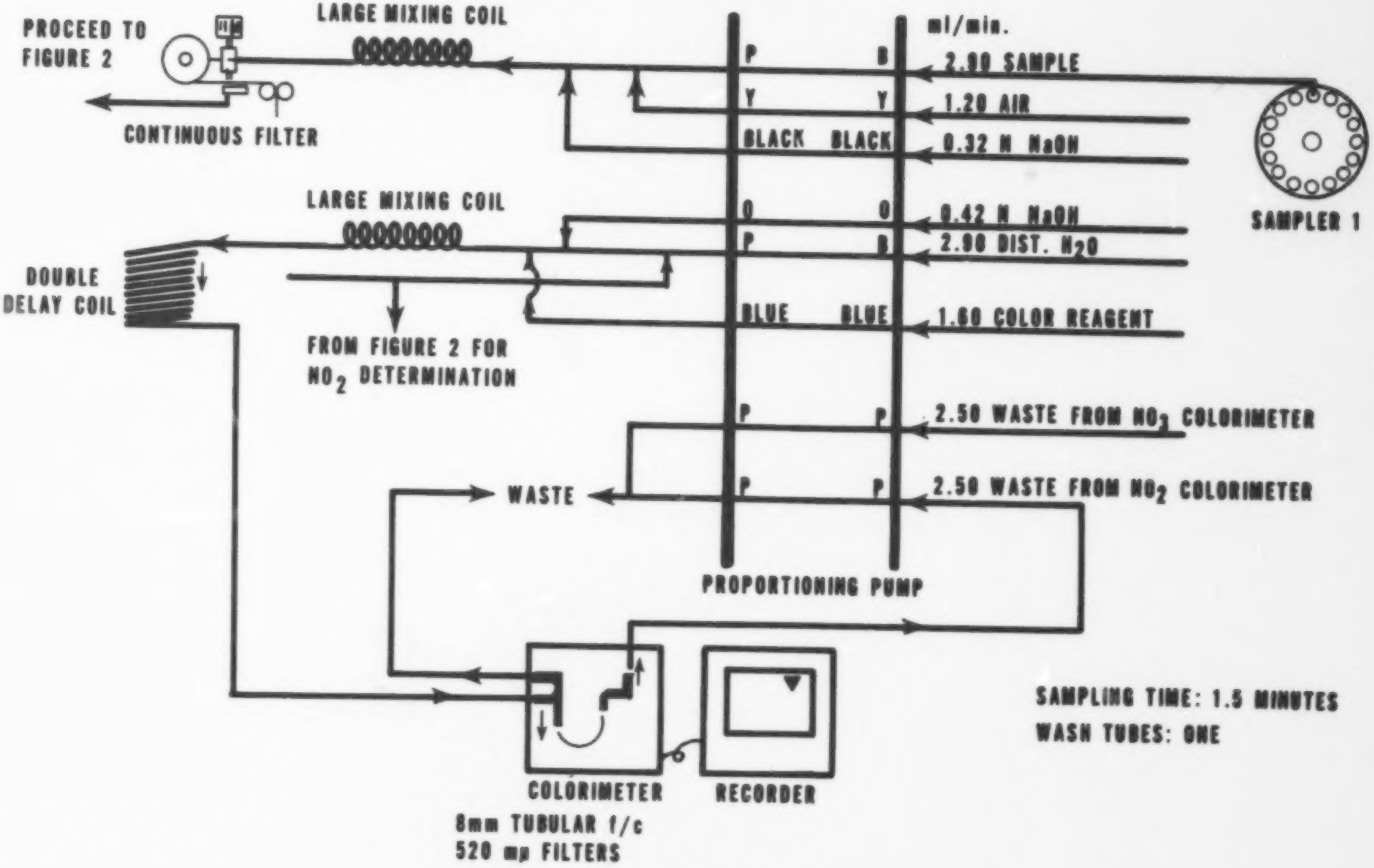
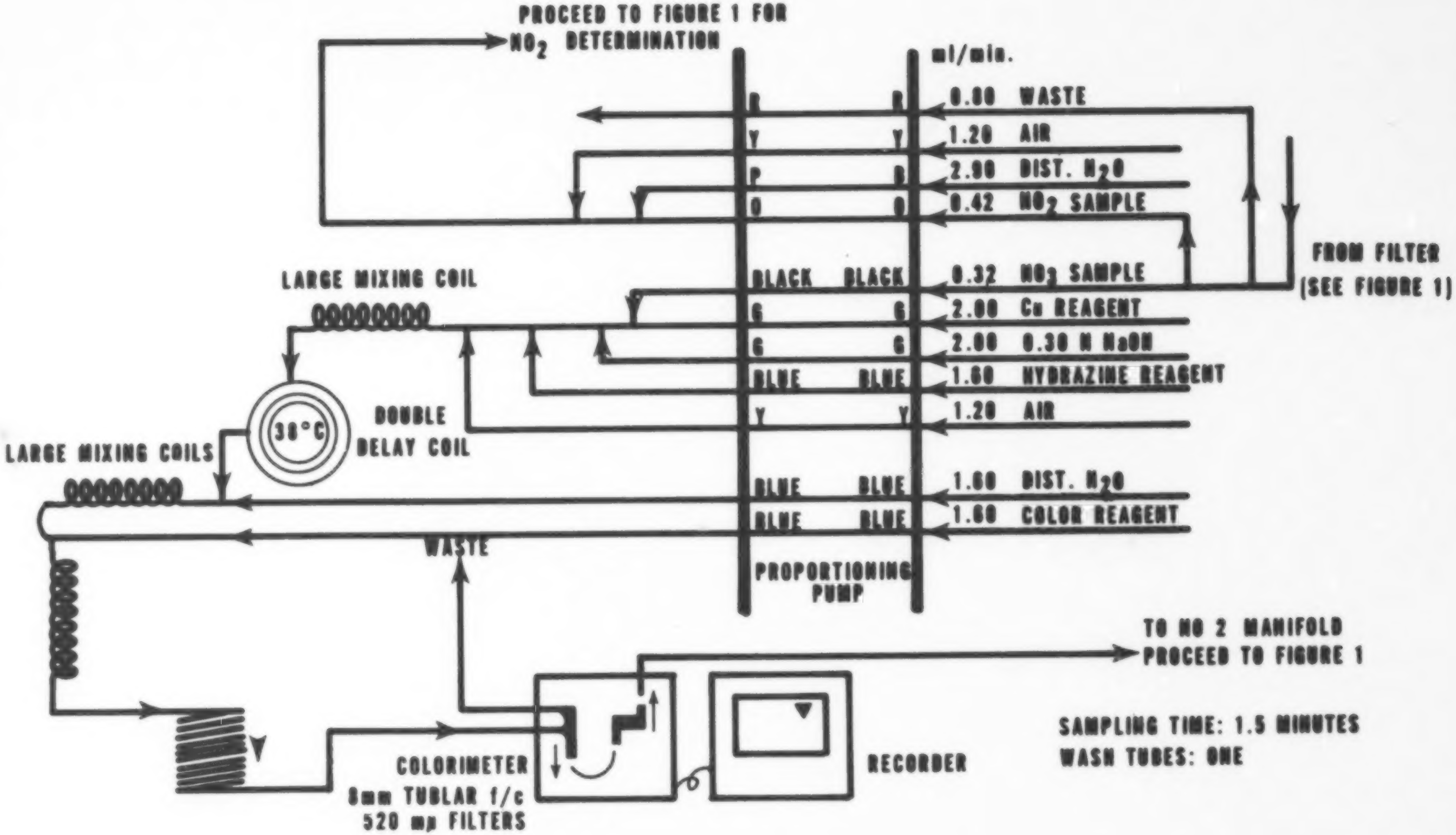

PROCEED TO FIGURE 2
CONTINUOUS FILTER
LARGE MIXING COIL
LARGE MIXING COIL
DOUBLE DELAY COIL
FROM FIGURE 2 FOR NO_2 DETERMINATION
WASTE
ml/min.
P
B
2.90 SAMPLE
Y
Y
1.20 AIR
BLACK
BLACK
0.32 N NaOH
O
O
0.42 N NaOH
P
B
2.90 DIST. H_2O
BLUE
BLUE
1.60 COLOR REAGENT
P
P
2.50 WASTE FROM NO_3 COLORIMETER
P
P
2.50 WASTE FROM NO_2 COLORIMETER
SAMPLER 1
PROPORTIONING PUMP
COLORIMETER
RECORDER
8mm TUBULAR f/c
520 mμ FILTERS
SAMPLING TIME: 1.5 MINUTES
WASH TUBES: ONE

FIGURE 1. NITRATE-NITRITE MANIFOLD

Preceding page blank


PROCEED TO FIGURE 1 FOR
NO_2 DETERMINATION
ml/min.
0.80 WASTE
1.20 AIR
2.90 DIST. H_2O
0.42 NO_2 SAMPLE
0.32 NO_3 SAMPLE
2.00 Cu REAGENT
2.00 0.30 N NaOH
1.60 HYDRAZINE REAGENT
1.20 AIR
1.60 DIST. H_2O
1.60 COLOR REAGENT
R
Y
P
O
BLACK
G
G
BLUE
Y
BLUE
BLUE
FROM FILTER
(SEE FIGURE 1)
LARGE MIXING COIL
DOUBLE
DELAY COIL
38°C
LARGE MIXING COILS
WASTE
PROPORTIONING
PUMP
TO NO 2 MANIFOLD
PROCEED TO FIGURE 1
COLORIMETER
8mm TUBLAR f/c
520 mμ FILTERS
RECORDER

SAMPLING TIME: 1.5 MINUTES
WASH TUBES: ONE

FIGURE 2. NITRATE-NITRITE MANIFOLD

NITROGEN, NITRATE-NITRITE

(Automated Cadmium Reduction Method)

1. Scope and Application

   1.1 This method pertains to the determination of nitrates and nitrites, singly or combined, present in surface and saline waters. The prescribed specifications permit analyses of samples in the range of 0.05 to 10 mg/liter, N present as NO_3.

2. Summary of Method(1)

   2.1 The initial step(2) is to reduce the nitrates to nitrites by using a cadmium-copper catalyst. The nitrites (those originally present plus reduced nitrates) are then reacted with sulfanilamide to form the diazo compound which is then coupled in an acid solution (pH 2.0 - 2.5) with N-1 naphthylethylenediamine hydrochloride to form the azo dye. The azo dye intensity, which is proportional to the nitrate concentration, is then measured. Separate rather than combined nitrate-nitrite values are readily obtainable by carrying out the procedure--first with, and then without, the initial Cd-Cu reduction step.

3. Sample Handling and Preservation

   3.1 Preservation by addition of 40 mg $HgCl_2$ per liter and refrigeration at 4°C is necessary.

Preceding page blank

4. Interferences

4.1 Ammonia and primary amines which are frequently present in natural waters may react to some extent with nitrites to form nitrogen. Thus, since, as in nature, the sample is not stable, the analyses should be performed as soon as possible.

4.2 In surface waters normally encountered in surveillance studies, the concentration of oxidizing or reducing agents and potentially interfering metal ions are well below the limits causing interferences. When present in sufficient concentration, metal ions may produce a positive error, i.e., Hg (II) and Cu (II), may form colored complex ions having absorption bands in the region of color measurement.

5. Apparatus

5.1 Technicon AutoAnalyzer consisting of the following components:

5.1.1 Sampler II.

5.1.2 Manifold (including Cu-Cd column).

5.1.3 Colorimeter equipped with 50 mm tubular flow cell and 540 mμ filters.

5.1.4 Range expander.

5.1.5 Recorder.

5.2 Cadmium-copper reduction column(2).

5.2.1 Preparation: Shake the 30 - 60 mesh av. diam. 0.5 mm cadmium turnings (Note 1) with a solution of 2% (wt/vol) copper sulfate pentahydrate solution. A weight of solution equal to 10 times the weight of the cadmium is used. The copper sulfate-treated cadmium catalyst is then placed in a 8 mm x 50 mm pyrex tubing and is followed by av. diam. 0.6 mm length 3.0 mm copper rods made from hydrogen treated copper wire (Note 2). The volume ratio of the cadmium bed to that of the copper should be about 3 - 1 to 4 - 1. (See Figure 1). Pyrex wool, inserted at the lower end of the reactor, is used to prevent the catalyst from dropping out of the reactor. The ends of the reactor are fabricated to accommodate the reactor into the system. The sample enters the column at the copper granule-packed end. To minimize back pressure due to a vertical position or channelling due to a horizontal position, the reductant tube is placed in an up-flow 20° incline.

Note 1 - Supplied by Technicon Corp., Ardsley, N.Y.

Note 2 - Supplied by F&M Scientific Corp., Avondale, Pa.

5.2.2 Regeneration: HCl, diluted 1 to 4, is pumped through the NH_4Cl line for one minute, followed by water for two minutes and then 2% copper sulfate solution for five minutes. For complete cleaning and coating, remove the column from the manifold. Using a small funnel and a short plastic connecting tube, the acid water and copper sulfate solution are successively poured into the column and allowed to flow through by gravity. The cadmium should ultimately acquire a moss-black appearance and the copper, a bright orange.

6. Reagents

6.1 Distilled water: Because of possible contamination, this should be prepared by passage through an ion exchange column comprised of amixture of both strongly acidic-cation and strongly basic-anion exchange resins. The regeneration of the ion exchange column should be carried out according to the instruction of the manufacturer.

6.2 Color reagent: To approximately 800 ml of distilled water, add, while stirring, 100 ml concentrated phosphoric acid, 40 g sulfanilamide, and 2 g N-1 naphthylethylenediamine dihydrochloride. Stir until dissolved and dilute to one liter. Store in brown bottle and keep in the dark when not in use. This solution is stable for several months.

6.3 Wash solution: Use distilled water for unpreserved samples; samples preserved with H_2SO_4, use 1 ml H_2SO_4 per liter of wash water.

6.4 Ammonium Chloride Solution (8.5% NH_4Cl): Dissolve 85 g of NH_4Cl reagent grade Ammonium Chloride in distilled water and dilute to one liter with distilled water. Add 1/2 ml Brij-35(4)

6.5 Stock nitrate solution: Dissolve 7.218 g KNO_3 and dilute to 1000 ml with distilled water. Preserve with 2 ml of chloroform per liter. Solution is stable for 6 months. 1 ml = 1.0 mg NO_3-N.

6.6 Stock nitrite solution: Dissolve 6.072 g KNO_2 and dilute to 1000 ml with distilled water. Solution is unstable; prepare as required. 1 ml = 1.0 mg NO_2-N.

6.7 Standard nitrate solution: Dilute 10.0 ml of stock nitrate solution to 1 liter. 1 ml = 0.01 mg NO_3-N. Preserve with 2 ml of chloroform per liter. Solution is stable for 6 months.

6.8 Standard nitrite solution: Dilute 10.0 ml of stock nitrite solution to 1 liter. 1 ml = 0.01 mg NO_2-N. Solution is unstable; prepare as required.

6.9 Using either standard nitrate solution or standard nitrite solution, prepare the following standards in 100.0-ml volumetric flasks:

Conc., mg NO_3-N or NO_2-N/l	Standard Solution/100 ml
0.0	0
0.05	0.5
0.10	1.0
0.20	2.0
0.50	5.0
1.00	10.0
2.00	20.0
4.00	40.0
6.00	60.0

Note: When the samples to be analyzed are saline waters, substitute Ocean Water (SOW) (5) should be used for preparing the standards; otherwise, distilled water is used. A tabulation of SOW composition follows:

NaCl - 24.53 g/l $MgCl_2$ - 5.20 g/l Na_2SO_4 - 4.09 g/l
$CaCl_2$ - 1.16 g/l   KCl - 0.70 g/l $NaHCO_3$ - 0.20 g/l
KBr - 0.10 g/l H_3BO_3 - 0.03 g/l $SrCl_2$ - 0.03 g/l
NaF - 0.003 g/l

7. Procedure

7.1 Set up the manifold as shown in Figure 2. Note that reductant column should be in 20° incline position with Cu at lower end.

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.3 Place appropriate nitrate and/or nitrite standards in sampler in order of decreasing concentration of nitrogen. Complete loading of sampler tray with unknown samples.

7.4 Switch sample line to sampler and start analysis.

8. Calculations

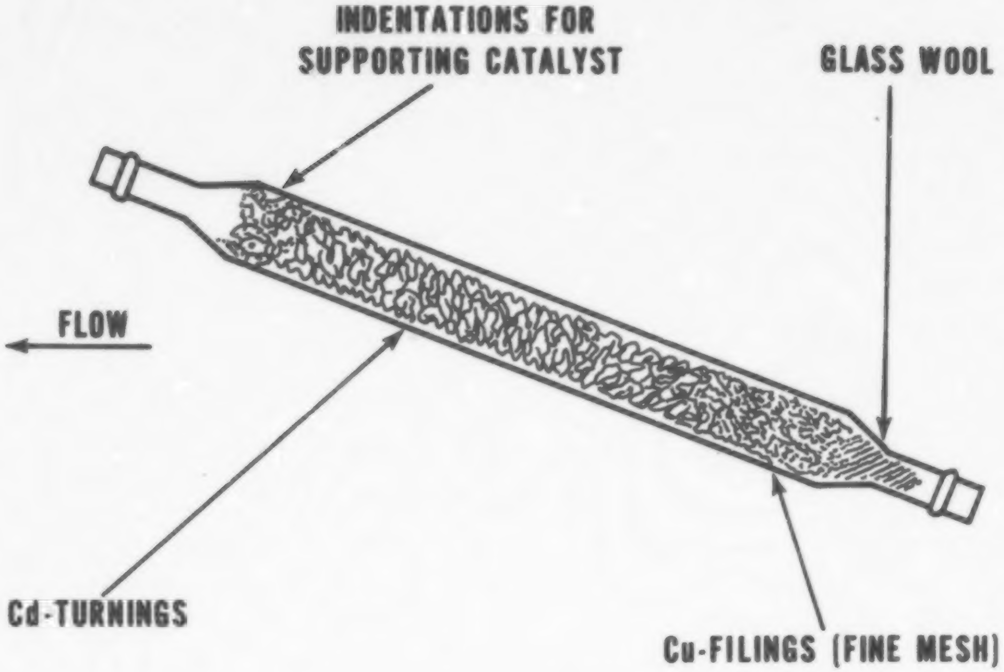
8.1 Prepare appropriate standard curve or curves derived from processing NO_3 and/or NO_2 standard through manifold. Compute concentration of samples by comparing sample peak heights with standard curve. Any sample whose computed concentration is less than 10% of its immediate predecessor must be rerun.

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

References

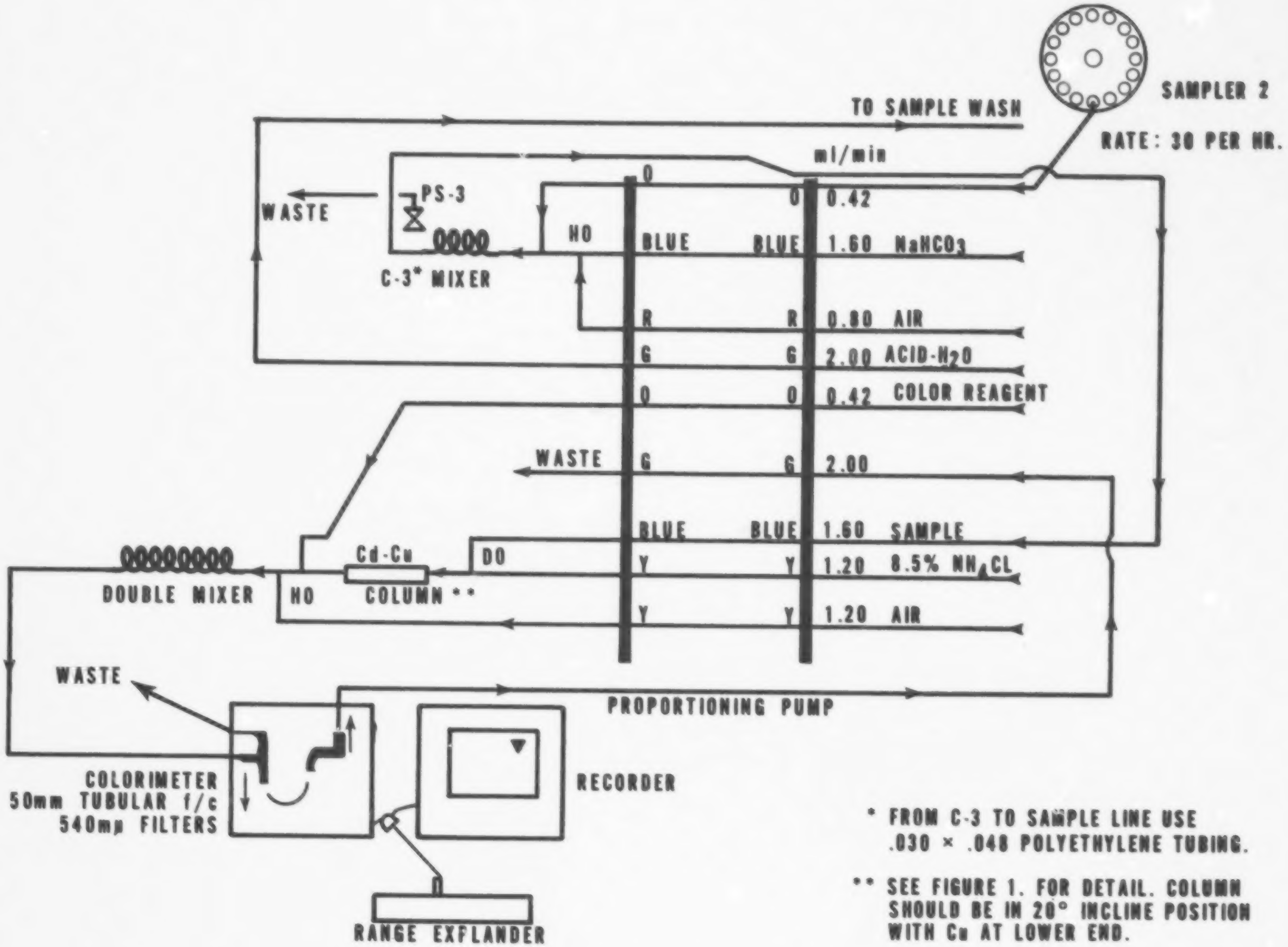
1. J.E. O'Brien and J. Fiore, "Automation in Sanitary Chemistry - parts 1 & 2 Determination of Nitrates and Nitrites." Wastes Engineering, 33, 128 & 238 (1962).
2. J.D. Strickland, C.R. Stearns, and F.A. Armstrong, "The Measurement of Upwelling and Subsequent Biological Processes by Means of the Technicon AutoAnalyzer and Associated Equipment." Deep Sea Research 14, 381-389 (1967).
3. "ASTM Manual on Industrial Water and Industrial Waste Water," Method D 1254, page 465 (1966).
4. Chemical Analyses for Water Quality Manual, Department of the Interior, FWPCA, R.A. Taft Sanitary Engineering Center Training Program, Cincinnati, Ohio 45226 (January 1966).
5. "ASTM Manual on Industrial Water and Industrial Waste Water," Substitute Ocean Water, Table 1, page 418, 1966 edition.


INDENTATIONS FOR SUPPORTING CATALYST
GLASS WOOL
FLOW
Cd-TURNINGS
Cu-FILINGS (FINE MESH)

TILT COLUMN TO 20° POSTION

FIGURE 1. CADMIUM-COPPER REDUCTION COLUMN
(1 1/2 ACTUAL SIZE)

Preceding page blank


SAMPLER 2
RATE: 30 PER HR.
TO SAMPLE WASH
ml/min
WASTE
PS-3
C-3* MIXER
HO
O
BLUE
R
G
O
G
BLUE
Y
Y
O
BLUE
R
G
O
G
BLUE
Y
Y
0.42
1.60 NaHCO3
0.80 AIR
2.00 ACID-H2O
0.42 COLOR REAGENT
WASTE
2.00
1.60 SAMPLE
1.20 8.5% NH4CL
1.20 AIR
Cd-Cu
COLUMN **
DO
HO
DOUBLE MIXER
WASTE
PROPORTIONING PUMP
COLORIMETER
50mm TUBULAR f/c
540mμ FILTERS
RECORDER
RANGE EXPLANDER

* FROM C-3 TO SAMPLE LINE USE .030 × .048 POLYETHYLENE TUBING.

** SEE FIGURE 1. FOR DETAIL. COLUMN SHOULD BE IN 20° INCLINE POSITION WITH Cu AT LOWER END.

FIGURE 2. NITRATE-NITRITE MANIFOLD

Preceding page blank

NITROGEN, NITRITE

1. Scope and Application

1.1 This method is applicable to the determination of nitrite in surface waters, domestic and industrial wastes, and saline waters.

1.2 The method is applicable in the range from 0.05 to 1.0 mg/l NO_2/N.

2. Summary of Method

2.1 The diazonium compound formed by diazotation of sulfanilamide by nitrite in water under acid conditions is coupled with N-(1-naphthyl)-ethenediamine to produce a reddish-purple color which is read in a spectrophotometer at 540 mμ.

3. Sample Handling and Preservation

3.1 Until more conclusive data is obtained, samples may be preserved by addition of 40 mg $HgCl_2$ per liter and stored at 4°C.

4. Interferences

4.1 There are very few known interferences at concentrations less than 1,000 times that of the nitrite; however, recent addition of strong oxidants or reductants to the samples will readily affect the nitrite concentrations. High alkalinity (>600 mg/l) will give low results due to a shift in pH of the color reaction.

Preceding page blank

5. Apparatus

5.1 Spectrophotometer equipped with 1.0 and 5.0 cm cuvettes for use at 540 mμ.

5.2 Nessler tubes, 50 ml or volumetric flasks, 50 ml.

6. Reagents

6.1 Distilled water free of nitrite and nitrate is to be used in preparation of all reagents and standards.

6.2 Buffer-color reagent. To 250-ml of distilled water, add 105-ml concentrated hydrochloric acid, 5.0 g sulfanilamide and 0.5 g N-1-Naphthylethylenediamine dihydrochloride. Stir until dissolved. Add 136 g of sodium acetate and again stir until dissolved. Dilute to 500 ml with distilled water. This solution is stable for several weeks if stored in the dark.

6.3 Nitrite-nitrogen stock solution, 1.0 ml = 0.10 mg NO_2-N. Dissolve 0.4926 g of dried anhydrous sodium nitrite, in distilled water and dilute to 1000 ml. Preserve with 2-ml chloroform per liter.

6.4 Nitrite-nitrogen standard solution, 1.0 ml = 0.001 mg NO_2-N. Dilute 10 ml of the stock solution to 1.0 liter.

7. Procedure

7.1 If the sample has a pH greater than 10 or a total alkalinity in excess of 600 mg/l adjust to approximately pH 6 with 1:3 HCl.

7.2 Filter the sample through a 0.45 μ pore size filter using the first portion of filtrate to rinse the filter flask.

7.3 Place 50 ml of sample, or an aliquot diluted to 50 ml in a 50-ml Nessler tube; hold until preparation of standards is completed.

7.4 At the same time prepare a series of standards in 50-ml Nessler tubes as follows:

ml of Standard Solution 1.0 ml = 0.001 mg NO_2-N	Conc., When Diluted to 50 ml, mg/l of NO_2-N
0.0 (Blank)	0.0
0.5	0.01
1.0	0.02
1.5	0.03
2.0	0.04
3.0	0.06
4.0	0.08
5.0	0.10
10.0	0.20

7.5 Add 2.0 ml of buffer-colored reagent to each standard and sample, mix and allow color to develop for at least 15 minutes. The color reaction medium should be between pH 1.5 and 2.0.

7.6 Read the color in the spectrophotometer at 540 mμ against the blank and plot concentration of NO_2-N against optical density.

8. Calculation

8.1 Read the concentration of NO_2-N directly from the curve.

8.2 Calculate the concentration of NO_2-N in the sample in milligrams per liter as follows:

$$NO_2\text{-N, mg/l} = \frac{\text{absorbance of sample x mg/l standard x 50}}{\text{absorbance of standard x ml sample}}$$

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

NITROGEN, ORGANIC + AMMONIA

(Automated Phenolate Method)

1. Scope and Application

1.1 This automated method is applicable to surface and saline waters. The applicable range is 1.0 to 10.0 mg N/l. Approximately 15 samples per hour can be analyzed.

2. Summary of Method

2.1 Organic nitrogen is determined by manually digesting the sample with potassium persulfate and sulfuric acid to convert the organic nitrogen, and any ammonia present, to ammonium sulfate. Subsequently, the automated phenol-hypochlorite procedure is used to measure the ammonia nitrogen. Nitrate-nitrite nitrogen is not measured by this procedure.

3. Sample Handling and Preservation

3.1 Preservation by addition of 40 mg $HgCl_2$ per liter and refrigeration at 4°C is necessary.

4. Interferences

4.1 No significant interferences.

5. Apparatus

5.1 Technicon AutoAnalyzer consisting of:

5.1.1 Sampler I.

5.1.2 Continuous Filter.

5.1.3 Manifold.

5.1.4 Proportioning Pump.

5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 650 mμ filters.

5.1.6 Recorder equipped with range expander.

5.2 Hot plate.

6. Reagents

6.1 Distilled Water: Special precaution must be taken to insure that distilled water is free of ammonia. Such water is prepared by passage of distilled water through an ion exchange column comprised of a mixture of both strongly acidic cation and strongly basic anion exchange resins. Since organic contaminants may interfere with this analysis, use of the resin Dowex XE-75 or equivalent which also tends to remove organic impurities is advised. The regeneration of the ion exchange column should be carried out according to the instructions of the manufacturer.

Note: All glassware must be pre-rinsed with this ammonia-free water to prevent contamination.

6.2 Sulfuric Acid: As it readily absorbs ammonia, special precaution must also be taken with respect to its use. Do not store bottles reserved for this determination in areas of potential ammonia contamination.

6.3 Potassium persulfate, low N (0.001%): Certain lots of this reagent do not meet this specification for nitrogen content. In order to insure this purity, dissolve 50 g of the reagent in 500 ml of distilled water at 60° to 70°C. Make alkaline with 10 ml of sodium hydroxide solution, 2.2M. Bubble air that has been passed through a 10% sulfuric acid solution through a tube which has been drawn into a capillary into the solution while withdrawing air from the solution, which is contained in a suction flask, under reduced pressure. Control the air flow so that a rather vigorous bubbling through the solution is maintained. After 30 minutes of vigorous bubbling, cool the solution overnight in a refrigerator at about 4°C. Filter the crop of crystals through a No. 40 Whatman filter paper previously washed with ammonia-free water. Wash the crystals with ice-cold ammonia-free water. Dry the crystals at 60 to 70°C and store in a tightly closed reagent bottle.

6.3 Sulfuric acid solution: Add slowly and with stirring 310 ml of reagent grade, concentrated sulfuric acid to 600 ml of ammonia-free water. Cool and dilute to 1,000 ml.

6.4 Phenol solution: Dissolve 83 g of phenol in 500 ml of ammonia-free water by stirring with a Teflon coated magnet for 10 minutes. Add 32 g NaOH and dilute to 1 liter.

6.5 Sodium hypochlorite solution: Dilute 250 ml of bleach solution containing 5.25% NaOCl to 500 ml with ammonia-free water.

6.6 Neutralizing solution: Dissolve 6 g EDTA disodium salt and 65 g of NaOH in 500 ml of distilled water. Dilute to 1,000 ml.

6.7 Stock solution: Dissolve 4.7168 g of ammonium sulfate analytical reagent in ammonia-free water and dilute to 1,000 ml. 1.0 ml = 1.00 mg N.

6.8 Standard solution: Dilute 10.0 ml of stock solution to 100.0 ml. 1 ml = 0.10 mg N.

6.8.1 Using standard solution, prepare the following standards in 100-ml volumetric flasks:

mg N/l	ml Standard Solution/100 ml
0.0	0
1.0	1.0
2.0	2.0
3.0	3.0
4.0	4.0
5.0	5.0
6.0	6.0
8.0	8.0
10.0	10.0

7. Procedure

7.1 Transfer a 25-ml sample of water to a 125-ml Erlenmeyer flask.

7.2 Add 3 ml of sulfuric acid solution and evaporate on a hot plate to light fumes of SO_3. This step may require approximately one hour. Close attention is not required of the sample; however, it should not be allowed to go to dryness. Cool the sample.

7.3 Add 1 ml of ammonia-free water and 1 g of potassium persulfate, low N, and swirl the flask.

7.4 Digest the sample on the hot plate for 15 minutes. Fumes of SO_3 should begin coming off after 7 minutes. The samples should become clear and transparent after this step, except in the presence of large amounts of silica. Cool the sample; dilute to 25 ml with ammonium free water. The sample is now ready for automatic analysis.

7.5 Set up manifold as shown in Figure 1.

7.6 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.7 Place distilled water wash tubes in alternate openings in Sampler and set sample timing at 2.0 minutes.

7.8 Arrange standards in Sampler in order of decreasing concentration. Complete loading of Sampler tray with unknown samples from 7.4

7.9 Switch sample line from distilled water to Sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed standards against concentration values. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

References

1. E. C. Julian and R. C. Kroner, "Determination of Organic Nitrogen in Water by Semi-Automatic Analysis," Automation in Analytical Chemistry, Technicon Symposia, 1966, Vol. 1, Mediad Inc., White Plains, N.Y. (1967), p 542.

2. D. D. Van Slyke and A. J. Hiller, Biol. Chem., 102, 499 (1933).

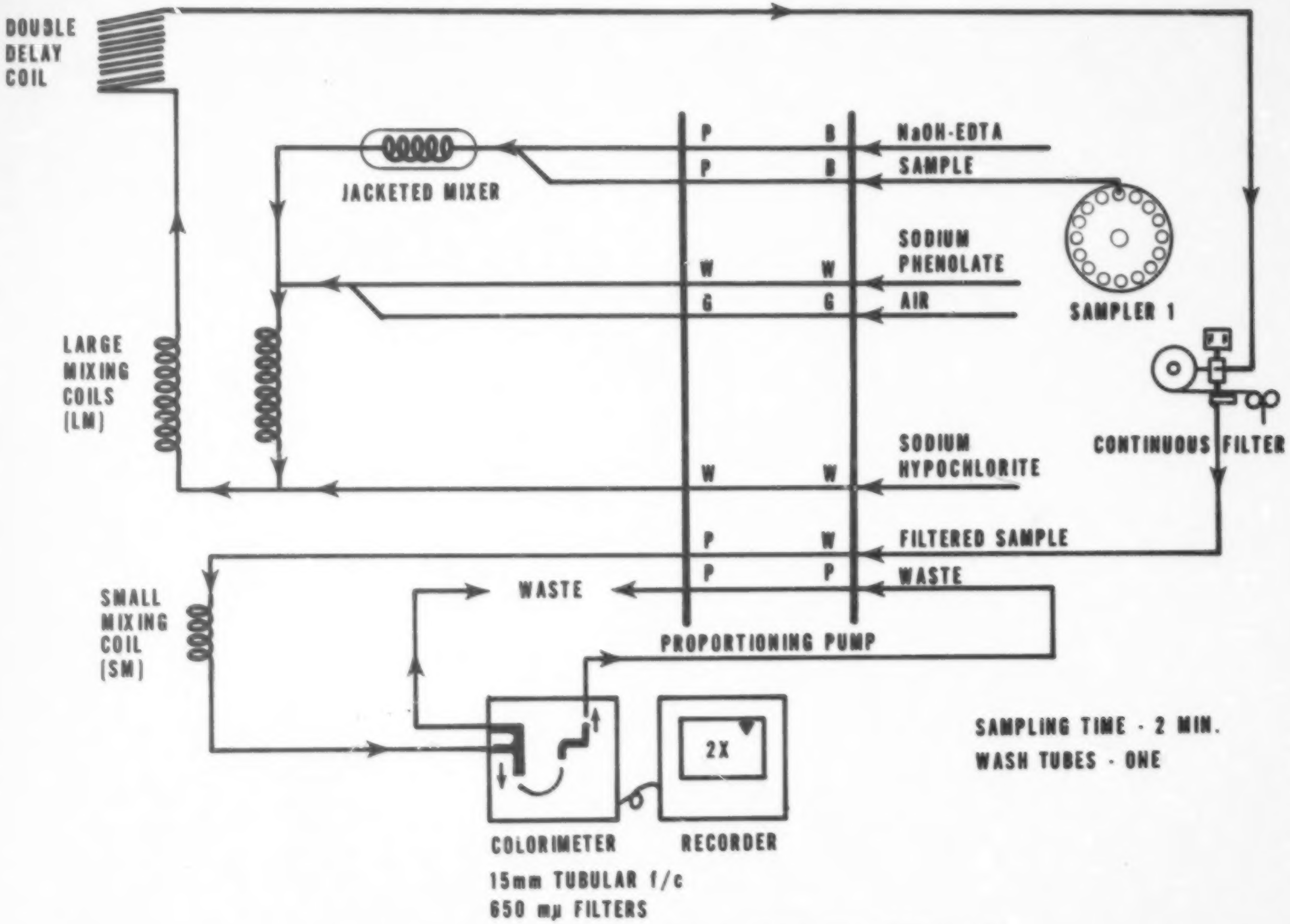

DOUBLE DELAY COIL
NaOH-EDTA
SAMPLE
P
P
B
B
JACKETED MIXER
SODIUM PHENOLATE
AIR
W
G
W
G
SAMPLER 1
LARGE MIXING COILS (LM)
CONTINUOUS FILTER
SODIUM HYPOCHLORITE
W
W
FILTERED SAMPLE
WASTE
P
P
W
P
WASTE
SMALL MIXING COIL (SM)
PROPORTIONING PUMP
2X
SAMPLING TIME - 2 MIN.
WASH TUBES - ONE
COLORIMETER
RECORDER
15mm TUBULAR f/c
650 mμ FILTERS

FIGURE 1 - ORGANIC NITROGEN & AMMONIA MANIFOLD

OIL AND GREASE

1. Scope and Application

1.1 This method includes the measurement of hexane extractable matter from waters, industrial wastes, and sewages. It is applicable to the determination of relatively non-volatile hydrocarbons, animal fats and waxes, grease and other types of greasy-oily matters.

1.2 The method is not applicable to measurement of light hydrocarbons that volatilize at temperatures below 80° C.

1.3 The method covers the range from 5 to 1000 mg/l of extractable material.

2. Summary of Method

2.1 The sample is acidified to a low pH (<3) and extracted with hexane using a Soxhlet extraction. The solvent is evaporated from the separated extract and the residue weighed.

3. Definitions

3.1 The definition of grease and oil is based on the procedure used. The source of the oil and/or grease, the solvent used, and presence of extractable non-oily matter will influence the material measured and interpretation of results.

Preceding page blank

4. Purity of Reagents

4.1 Reagent grade hexane shall be used.

5. Sampling and Storage

5.1 A representative sample should be collected in a wide-mouth bottle marked at the 1 liter volume. The initial step of acidification shall be carried out in the sample bottle. The entire sample is used for the test.

5.2 Because losses of grease will occur on sampling equipment, collection of a composite sample is impractical, and the examination of individual portions collected at prescribed time intervals must be used to obtain the average concentration over an extended period.

6. Apparatus

6.1 Extraction apparatus consisting of:

6.1.1 Soxhlet Extractor, medium size (Corning No. 3740 or equivalent).

6.1.2 Soxhlet thimbles, to fit in Soxhlet Extractor, 6.1.1.

6.1.3 Flask, 125 ml (Corning No. 4100 or equivalent).

6.1.4 Condenser, Allihn (bulb) type, to fit extractor.

6.2 Vacuum pump, or other source of vacuum.

6.3 Buchner funnel, 12 cm.

7. Reagents

7.1 Hydrochloric acid - Conc. (sp. g 1.18).

7.2 N-Hexane, b.p. 69° C.

7.3 Filter paper, Whatman No. 40, 11 cm.

7.4 Muslin cloth discs, 11 cm.

7.5 Diatomaceous - silica filter aid suspension, 10 g/l distilled water.

Note 1 - Hyflo Super-Cel (Johns-Manville Corp.) or equivalent is used in the preparation of the filter aid suspension.

8. Procedure

8.1 In the following procedure, all steps must be rigidly adhered to if consistent results are to be obtained.

8.2 Acidify the 1 liter sample to pH <3, which generally requires 5 ml of conc. HCl. Use of a pH sensitive paper is recommended when checking the pH of the sample.

8.3 Prepare a filter consisting of a muslin cloth disc overlaid with filter paper. Place the assembled filter in the Buchner funnel and wet the filter, pressing down the edges to secure a seal. Using a vacuum, add 100 ml of the filter aid suspension through the filter and then wash with 3-100 ml volumes of distilled water. Continue the vacuum until no more water passes through the filter.

8.4 Filter the acidified sample under vacuum and again continue the vacuum until no more water passes through the filter.

8.5 Remove the filter paper to a watch glass by means of forceps. Add the material adhering to the edges of the muslin cloth disc. Wipe the sides and bottom of the collecting vessel, the stirring rod, and the Buchner funnel with pieces of filter paper soaked in hexane. Care must be taken to remove all films due to grease and to collect all solid material. Add all pieces of filter paper to the paper on the watch glass. Roll the filter paper and the pieces of filter paper and fit into a paper extraction thimble. Wipe the watch glass with a piece of filter paper soaked in hexane and place in the extraction thimble.

8.6 Dry the extraction thimble containing the filter paper in an oven at 103° C for exactly 30 minutes. Fill the thimble with small glass beads or glass wool.

8.7 Weigh the extraction flask, add the hexane, and connect to the Soxhlet apparatus in which the extraction thimble has been placed. Extract at the rate of 20 cycles per hour for four hours. The four hours is timed from the first cycle.

8.8 Distill the solvent from the extraction flask in a water bath at 85° C. Dry by placing the flask on a steam bath and draw air through the flask by means of an applied vacuum for 15 minutes.

8.9 Cool in a desiccator for 30 minutes and weigh.

9. Calculation

9.1 $$\text{mg/l total grease} = \frac{\text{mg increase in weight of flask} \times 1{,}000}{\text{ml sample}}$$

10. Precision and Accuracy

10.1 Precision and accuracy data are not available.

ORGANIC CARBON, TOTAL AND DISSOLVED

1. Scope and Application

1.1 This method includes the measurement of organic carbon in surface waters, domestic and industrial wastes, and saline waters. Exclusions are noted under Definitions and Interferences.

1.2 The method is applicable to measurement in the range of 1 to 150 mg/liter.

2. Summary of Method

2.1 A micro sample of the wastewater to be analyzed is injected into a catalytic combustion tube which is enclosed by an electric furnace thermostated at 950°C. The water is vaporized and the carbonaceous material is oxidized to carbon dioxide (CO_2) and steam in a carrier stream of pure oxygen. The oxygen flow carries the steam and CO_2 out of the furnace where the steam is condensed and the condensate removed. The CO_2, oxygen, and remaining water vapor enter an infrared analyzer sensitized to provide a measure of CO_2. The amount of CO_2 present is directly proportional to the concentration of carbonaceous material in the injected sample.

3. Definitions

3.1 The carbonaceous analyzer measures all of the carbon in a sample after injection into the combustion tube. Because

Preceding page blank

of various properties of carbon-containing compounds in liquid samples, preliminary treatment of the sample prior to injection dictates the definition of the carbon as it is measured.

Forms of carbon that are measured by the combustion-infrared method are:

A) soluble, nonvolatile organic carbon; for instance, natural sugars

B) soluble, volatile organic carbon; for instance, mercaptans

C) insoluble, partially volatile carbon; for instance, oils

D) insoluble, particulate carbonaceous materials; for instance, cellulose fibers

E) soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter; for instance, oily matter adsorbed on silt particles

3.2 The final usefulness of the carbon measurement is in assessing the potential oxygen-demanding load of organic material on a receiving stream. This statement applies whether the carbon measurement is made on a sewage plant effluent, industrial waste, or on water taken directly from the stream. In this light, carbonate and bicarbonate carbon are not a part of the oxygen demand in the stream and therefore should be discounted in the final calculation or removed prior to analysis. The manner of preliminary treatment therefore defines the types of carbon which are measured.

4. Sample Handling and Preservation

4.1 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples (Note 1).

Note 1 - A brief study performed in the AQC Laboratory indicated that distilled water stored in new, one quart cubitainers did not show any increase in organic carbon after two weeks exposure.

4.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

4.3 In instances where analysis cannot be performed within two hours (2 hours) from time of sampling, it is recommended that the sample be acidified ($pH \leq 2$) with HCl.

5. Interferences

5.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

5.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter type syringe. The needle openings of the syringe limit the maximum size of particles which may be included in the sample. (Cf 6.3)

6. Apparatus

6.1 Apparatus for blending or homogenizing samples: Generally, a Waring-type blender is satisfactory.

6.2 Apparatus for total and dissolved organic carbon:

6.2.1 Dow-Beckman Carbonaceous Analyzer, (single channel) or

6.2.2 Dow Beckman Carbonaceous Analyzer Model No. 915 (dual channel).

6.3 Hypodermic syringe, 0-50 µl, needle opening of approximately 150 microns; Hamilton No. 705 N or equivalent is satisfactory.

6.3.1 Hamilton No. 750 N, 0-500 µl has a needle opening of approximately 400 microns and may be used for samples containing large particulates.

7. Reagents and Materials

7.1 Distilled water used in preparation of standards and for dilution of samples should be ultra pure to reduce the size of the blank. Carbon dioxide-free, double distilled water is recommended. Ion exchanged waters are not recommended because of the possibility of contamination with organic materials from the resins.

7.2 Potassium Hydrogen Phthalate, stock solution, 1000 mg carbon/liter: Dissolve 0.2128 g of potassium hydrogen phthalate (Primary Standard Grade) in double distilled water and dilute to 100.0 ml.

Note: Sodium oxalate and acetic acid are not recommended as stock solutions.

7.3 Potassium Hydrogen Phthalate, standard solutions: Prepare standard solutions from the stock solution with double distilled water as follows:

ml of Stock Solution Diluted to 100 ml	Standard mg C/liter
1.0	10
2.0	20
3.0	30
4.0	40
5.0	50
6.0	60
8.0	80
10.0	100

7.4 Carbonate-bicarbonate, stock solution, 1000 mg carbon/liter: Weigh 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate and transfer both to the same 100 ml volumetric flask. Dissolve with double distilled water.

7.5 Carbonate-bicarbonate, standard solution: Prepare a series of standards similar to 7.3.

7.6 Blank solution: Use the same distilled water (or similar quality water) used for the preparation of the standard solutions.

7.7 **Packing for total carbon tube.** Dissolve 20 g of $Co(NO_3)_2.6H_2O$ (cobalt nitrate hexahydrate) in 50 ml of distilled water. Add this solution to 15 grams of long-fiber asbestos in a porcelain evaporating dish. Mix and evaporate to dryness on a steam bath. Place the dish in a cold muffle furnace and bring to a temperature of 950°C. After one to two hours at this temperature, remove the dish and allow to cool. Break up any large lumps and mix adequately but not excessively.

With the combustion tube held in a vertical position, taper joint up, put about 1/2" of untreated asbestos in the tube first, then transfer, in small amounts, approximately one gram of catalyst into the tube with forceps or tweezers. As it is added, tap or push the material gently with a 1/4" glass rod. Do not force the packing. The weight of the rod itself is sufficient to compress the material. When completed, the length of the packing should be about five or six centimeters.

Test the packed tube by measuring the flow rate of gas through it at room temperature, and then at 950°C. The rate should not drop more than 20%.

7.8 **Packing for carbonate tube, (dual channel instrument).** Place a small wad of quartz wool or asbestos near the exit end of the carbonate evolution tube. From the entrance end add 6-12 mesh quartz chips, allowing these to collect against the wad to a length of 10 cm. Pour an excess of 85 percent phosphoric acid into the tube while holding it vertically, and allow the excess to drain out.

8. Instrument Adjustment

8.1 Turn on the infrared analyzer, recorder, and tube furnaces, setting the total carbon furnace at 950°C and the carbonate furnace at 175°C. Allow a warm-up time of at least 2 hr. for attainment of stable operation; in daily use the analyzer can be left on continuously. Adjust the oxygen flow rate to 80 to 100 ml/min through the total carbon tube. With the recorder set at the 5-mv range, adjust the amplifier gain so that a 20-μl sample of the 100 mg/liter carbon standard gives a peak height of approximately half the recorder scale (see 7.3). At this setting the noise level should be less than 0.5 percent of full scale. If the noise level is higher, the analyzer or the recorder may require servicing.

8.2 Immediately prior to carrying out calibrations or analyses, inject several portions of the appropriate 100 mg/liter standard (see 7.2) into the tube to be used, until constant readings are obtained.

9. Calibration - Dual Channel Instrument

9.1 Successively introduce 20 μl of each phthalate standard into the total carbon tube and read the height of the corresponding peak. Between injections allow the recorder pen to return to its base line. The actual injection technique is as follows: Rinse the syringe several times with the solution to be analyzed, fill, and adjust to 20 μl. Wipe off the excess with soft paper tissue, taking care that no lint adheres to the needle. Remove the plug from the syringe holder, insert the sample syringe, and inject the sample into the combustion tube with a single, rapid movement of the index finger. Leave the syringe in the holder until the flow rate returns to normal, then replace it with the plug. Run duplicate determinations on each solution and on a water blank.

9.2 Correct standards for blank correction as follows: Standard peak height minus blank peak height = correct peak height in mm. Prepare a standard curve of total carbon versus peak height.

9.3 In the same way, prepare a series of diluted carbonate standards containing 20, 40, 60, 80, and 100 mg of inorganic carbon per liter. Turn the four-way valve of the apparatus to direct the gas flow through the low temperature tube and to the analyzer. Adjust the flow rate to 80 to 100 ml/min and allow the baseline to become stabilized. Successively introduce 20 µl of each standard and a water blank in duplicate into the low temperature tube and read the peak heights as previously described.

9.4 Prepare a standard curve of inorganic carbon versus peak height applying the correction as noted in 9.2.

10. Procedure - Dual Channel Instrument

10.1 Mix or blend each sample thoroughly and carry out any appropriate dilution to bring the carbon content within the range of the standard curve.

10.2 Following the technique described in 9.1 and 9.3, inject 20-µl samples successively (in duplicate) into each tube and read the peak heights corresponding to total carbon and inorganic (carbonate) carbon. From the appropriate calibration curve and each peak height observed, read the corresponding carbon concentration in mg/liter.

10.3 Subtract the inorganic carbon value from the total carbon value. The difference thus obtained is operationally defined as Total Organic Carbon.

10.4 Filter a 100 ml aliquot through a pre-rinsed 0.45 µ pore size filter. Repeat sample injection as in 10.2.

10.5 Subtract the dissolved inorganic carbon value from the dissolved carbon value. The difference thus obtained is operationally defined as Dissolved Organic Carbon.

11. Calibration - Single Channel Instrument

11.1 Standardize the instrument according to directions given in 9.1 and 9.2.

12. Procedure - Single Channel Instrument

12.1 Transfer a representative aliquot of about 10 - 15 ml to a 30 ml beaker, add 2 or more drops of concentrated HCl until the pH is reduced to $\leq$ 2 and purge with CO_2-free nitrogen gas for about 5 - 10 minutes. (Do not use plastic tubing). Place the beaker on a magnetic stirrer and while stirring withdraw a 20 µl sample. Inject the sample as in 9.1.

12.2 Obtain concentration directly from standard curve. The carbon thus measured is operationally defined as Total Organic Carbon.

12.3 Filter a 100-ml aliquot through a pre-rinsed 0.45 µ pore size filter and proceed as in 12.1.

12.4 Obtain concentration directly from standard curve. The carbon thus measured is operationally defined as Dissolved Organic Carbon.

13. Precision and Accuracy

13.1 The precision of this method as determined by ASTM is expressed as follows:

$S_L = 0.032\, x + 0.03$ where

S_L = single laboratory precision and

x = concentration of carbon in mg/l

PHOSPHORUS, ALL FORMS

(Single Reagent Method)

1. Scope and Application

1.1 These methods cover the determination of specified forms of phosphorus in surface waters, domestic and industrial wastes, and saline waters. They may be applicable to sediment-type samples, sludges, algal blooms, etc., but sufficient data is not available at this time to warrant such usage when measurements for phosphorus content are required.

1.2 The methods are based on reactions that are specific for the orthophosphate ion. Thus, depending on the prescribed pre-treatment of the sample, the various forms of phosphorus given in Figure 1 may be determined. These forms are, in turn, defined in Table 1.

1.2.1 Except for in-depth and detailed studies, the most commonly measured forms are phosphorus and dissolved phosphorus, and orthophosphate and dissolved orthophosphate. Hydrolyzable phosphorus is normally found only in sewage-type samples and insoluble forms of phosphorus, as noted, are determined by calculation.

1.3 The methods are usable in the 0.01 to 0.5 mg/l P range.

Preceding page blank

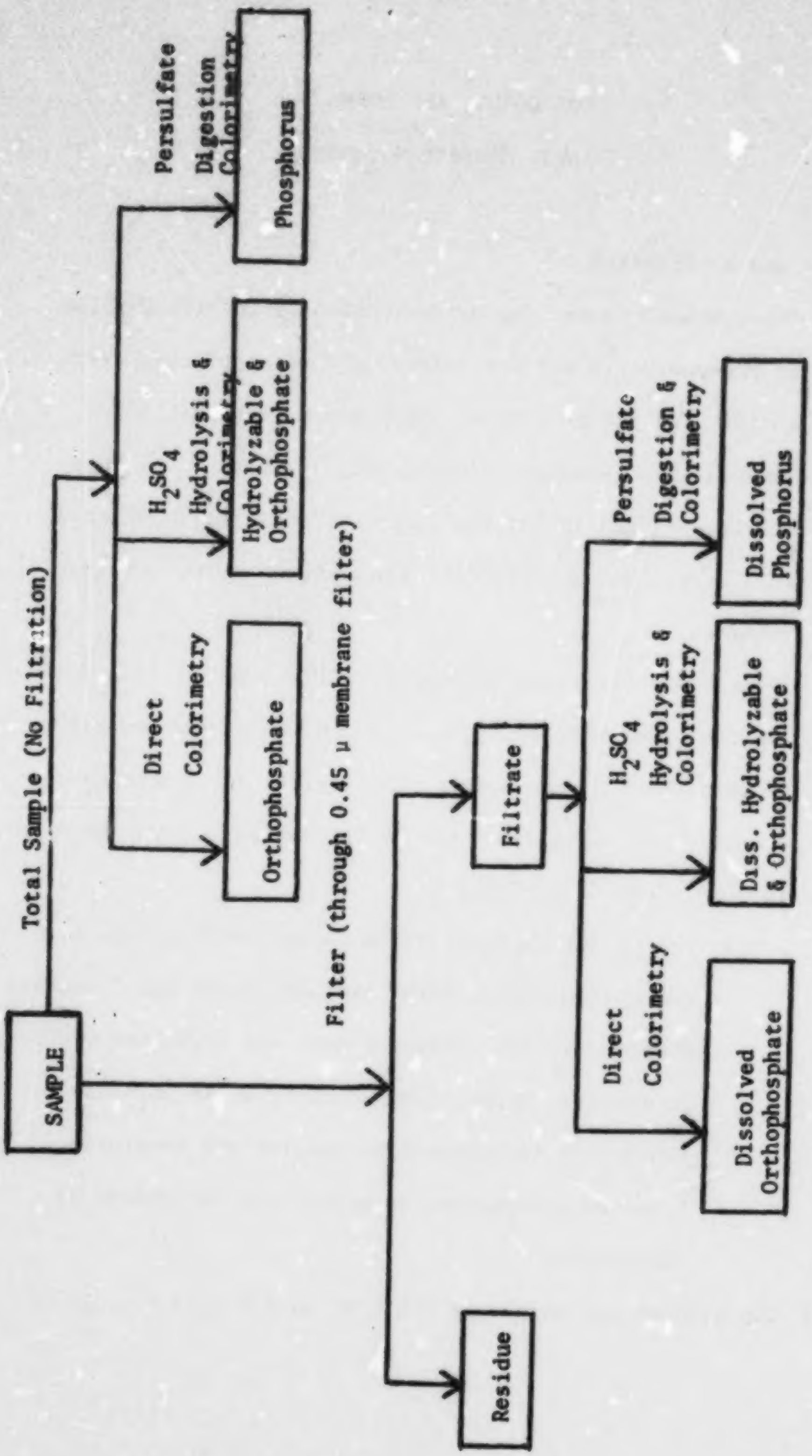

SAMPLE
Total Sample (No Filtration)
Direct
Colorimetry
Orthophosphate
H_2SO_4
Hydrolysis &
Colorimetry
Hydrolyzable &
Orthophosphate
Persulfate
Digestion
Colorimetry
Phosphorus
Filter (through 0.45 µ membrane filter)
Filtrate
Direct
Colorimetry
Dissolved
Orthophosphate
H_2SO_4
Hydrolysis &
Colorimetry
Diss. Hydrolyzable
& Orthophosphate
Persulfate
Digestion &
Colorimetry
Dissolved
Phosphorus
Residue

Figure 1. Analytical Scheme for Differentiation of Phosphorus Forms.

2. Summary of Method

2.1 Ammonium molybdate and potassium antimonyl tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phosphate-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.

2.2 Only orthophosphate forms a blue color in this test. Polyphosphates (and some organic phosphorus compounds) may be converted to the orthophosphate form by sulfuric-acid-hydrolysis. Organic phosphorus compounds may be converted to the orthophosphate form by persulfate digestion.(2)

3. Definitions

3.1 The various forms of phosphorus are defined in Table 1.

4. Sample Handling and Preservation

4.1 If benthic deposits are present in the area being sampled, great care should be taken not to include these deposits.

4.2 Sample containers may be of plastic material, such as cubitainers, or of Pyrex glass.

4.3 If the analysis cannot be performed the same day of collection, the sample should be preserved by the addition of 40 mg $HgCl_2$ per liter and refrigeration at 4° C.

TABLE 1

PHOSPHORUS TERMINOLOGY

1. Phosphorus (P) - all of the phosphorus present in the sample, regardless of form, as measured by the persulfate digestion procedure.
   a. Orthophosphate (P, ortho) - inorganic phosphorus $[(PO_4)^{-3}]$ in the sample as measured by the direct colorimetric analysis procedure.
   b. Hydrolyzable Phosphorus (P, hydro) - phosphorus in the sample as measured by the sulfuric acid hydrolysis procedure, and minus pre-determined orthophosphates. This hydrolyzable phosphorus includes polyphosphates $[(P_2O_7)^{-4}$, $(P_3O_{10})^{-5}$, etc.] + some organic phosphorus.
   c. Organic Phosphorus (P, org) - phosphorus (inorganic + oxidizable organic) in the sample as measured by the persulfate digestion procedure, and minus hydrolyzable phosphorus and orthophosphate.
2. Dissolved Phosphorus (P-D) - all of the phosphorus present in the filtrate of a sample filtered through a phosphorus-free filter of 0.45 micron pore size and measured by the persulfate digestion procedure.
   a. Dissolved Orthophosphate (P-D, ortho) - as measured by the direct colorimetric analysis procedure.
   b. Dissolved Hydrolyzable Phosphorus (P-D, hydro) - as measured by the sulfuric acid hydrolysis procedure and minus pre-determined dissolved orthophosphates.

TABLE 1 (Continued)

c. Dissolved Organic Phosphorus (P-D, org) - as measured by the persulfate digestion procedure, and minus dissolved hydrolyzable phosphorus and orthophosphate.

3. The following forms, when sufficient amounts of phosphorus are present in the sample to warrant such consideration, may be calculated:

   a. Insoluble Phosphorus (P-I) = (P) - (P-D).

      (1) Insoluble orthophosphate (P-I, ortho) = (P, ortho) - (P-D, ortho).

      (2) Insoluble Hydrolyzable Phosphorus (P-I, hydro) = (P, hydro) - (P-D, hydro).

      (3) Insoluble Organic Phosphorus (P-I, org) = (P, org) - (P-D, org).

4. All phosphorus forms shall be reported as P, mg/l.

5. Interferences

5.1 It is reported(1) that no interference is caused by copper, iron, or silicate at concentrations many times greater than their greatest reported concentration in sea water. However, high iron concentrations can cause precipitation of phosphorus through the formation of clumps in the bottom of the sample.

5.2 The salt error for samples ranging from 5 to 20 percent salt content was found to be less than 1 percent(1).

5.3 Arsenate, in concentrations greater than found in sea water, does not interfere(1)

6. Apparatus

6.1 Photometer - A spectrophotometer or filter photometer suitable for measurements at 880 mμ, and providing a light path of 1 inch (2.54 cm) or longer, should be used.

6.2 Acid-washed glassware: All glassware used in the determination should be washed with hot 1:1 HCl and rinsed with distilled water. The acid-washed glassware should be filled with distilled water and treated with all the reagents to remove the last traces of phosphorus that might be adsorbed on the glassware. Preferably, this glassware should be used only for the determination of phosphorus and after use it should be rinsed with distilled water and kept covered until needed again. If this is done, the treatment with 1:1 HCl and reagents is only required occasionally. Commercial detergents should never be used.

7. Reagents

7.1 Sulfuric acid solution, 5N: Dilute 70 ml of conc. H_2SO_4 with distilled water to 500 ml.

7.2 Potassium antimonyl tartrate solution: Weigh 1.3715 g $K(SbO)C_4H_4O_6.1/2\ H_2O$, dissolve in 400 ml distilled water in 500 ml volumetric flask, dilute to volume. Store in glass-stoppered bottle.

7.3 Ammonium molybdate solution: Dissolve 20 g $(NH_4)_6Mo_7O_{24}.{}^4\ H_2O$ in 500 ml distilled water. Store in a plastic bottle at 4° C.

7.4 Ascorbic acid, 0.1M: Dissolve 1.76 g of ascorbic acid in 100 ml of distilled water. The solution is stable for about a week if stored at 4° C.

7.5 Combined reagent: Mix the above reagents in the following proportions for 100 ml of the mixed reagent: 50 ml of 5N H_2SO_4, 5 ml of potassium antimonyl tartrate solution, 15 ml of ammonium molybdate solution, and 30 ml of ascorbic acid solution. Mix after addition of each reagent. All reagents must reach room temperature before they are mixed and must be mixed in the order given. If turbidity forms in the combined reagent, shake and let it stand for a few minutes until the turbidity disappears before proceding. The reagent is stable for one week if stored at 4° C.

7.6 Strong-acid solution: Slowly add 310 ml conc. H_2SO_4 to 600 ml distilled water. When cool, dilute to 1 liter.

7.7 Ammonium persulfate.

7.8 Stock Solution: Dissolve in distilled water 0.2197 g of potassium dihydrogen phosphate, KH_2PO_4, which has been dried in an oven at 105° C. Dilute the solution to 1,000 ml; 1.00 ml equals 0.05 mg P.

7.9 Standard Solution: Dilute 10.0 ml of stock phosphorus solution to 1,000 ml with distilled water; 1.00 ml equals 0.5 µg P.

7.9.1 Using standard solution, prepare the following standards in 50.0-ml volumetric flasks:

ml of Standard Solution	Conc., mg/l
0	0.00
1.0	0.01
3.0	0.03
5.0	0.05
10.0	0.10
20.0	0.20
30.0	0.30
40.0	0.40
50.0	0.50

8. Procedure

8.1 Phosphorus

8.1.1 Add 1 ml of strong-acid solution to a 50 ml sample in a 125-ml Erlenmeyer flask.

8.1.2 Add 0.4 gram of ammonium persulfate.

8.1.3 Boil gently on a pre-heated hot plate for approximately 30-40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121° C (15-20 psi).

8.1.4 Add phenolphthalein and adjust sample to pink with IN NaOH. Bring back to colorless with one drop strong-acid solution. Cool and dilute the sample to 50 ml.

8.1.5 Determine phosphorus as outlined in 8.3.2 Orthophosphate.

8.2 Hydrolyzable Phosphorus

8.2.1 Add 1 ml of strong-acid solution to a 50-ml sample in a 125-ml Erlenmeyer Flask.

8.2.2 Boil gently on a pre-heated hot plate for 30-40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121° C (15-20 psi).

8.2.3 Add phenolphthalein and adjust sample to pink with 1 N NaOH. Bring back to colorless with one drop strong-acid solutions. Cool and dilute the sample to 50 ml.

8.2.4 The sample is now ready for determination of phosphorus as outlined in 8.3.2 Orthophosphate.

8.3 Orthophosphate

8.3.1 Add 1 drop of phenolphthalein indicator to the 50.0 ml sample. If a red color develops, add strong-acid solution drop-wise to just discharge the color.

8.3.2 Add 8.0 ml of combined reagent to sample and mix thoroughly. After a minimum of ten minutes, but no longer than thirty minutes, measure the color absorbance of each sample at 880 mμ with a spectrophotometer, using the reagent blank as the reference solution.

9. Calculation

9.1 Prepare standard curve by plotting absorbance values of standards as ordinates and the corresponding phosphorus concentrations as abscissas.

9.1.1 Process standards and blank exactly as the samples. Run at least a blank and two standards with each series of samples. If the standards do not agree within ± 2% of the true value, prepare a new calibration curve.

9.2 Obtain concentration value of sample directly from prepared standard curve. Report results as P, mg/l.

10. Precision and Accuracy

10.1 In eight laboratories involving 13 analysts, using a variety of natural water samples, both salt and fresh, the standard deviation at a concentration of 0.23 mg P/l was ± 0.004 (AQC Laboratory).

10.2 Under the same conditions, recovery was 101% (AQC Laboratory).

References

1. J. Murphy and J. Riley, "A Modified Single Solution Method for the Determination of Phosphate in Natural Waters." Anal. Chim. Acta., 27, 31 (1962).

2. M. Gales, Jr., E. Julian, and R. Kroner, "Method for Quantitative Determination of Total Phosphorus in Water." Jour AWWA, 58, No. 10, 1363 (1966).

PHOSPHORUS, ALL FORMS

(Automated Single Reagent Method)

1. Scope and Application

1.1 These methods cover the determination of specified forms of phosphorus in surface waters, domestic and industrial wastes, and saline waters. They may be applicable to sediment-type samples, sludges, algal blooms, etc., but sufficient data is not available at this time to warrant such usage when measurements for phosphorus content are required.

1.2 The methods are based on reactions that are specific for the orthophosphate ion. Thus, depending on the prescribed pre-treatment of the sample, the various forms of phosphorus given in Figure 1 may be determined. These forms are, in turn, defined in Table 1.

1.2.1 Except for in-depth and detailed studies, the most commonly measured forms are phosphorus and dissolved phosphorus, and orthophosphate and dissolved orthophosphate. Hydrolyzable phosphorus is normally found only in sewage-type samples and insoluble forms of phosphorus, as noted, are determined by calculation.

1.3 The methods are usable in the 0.01 to 1.0 mg P/1 range. Approximately 20 samples per hour can be analyzed.

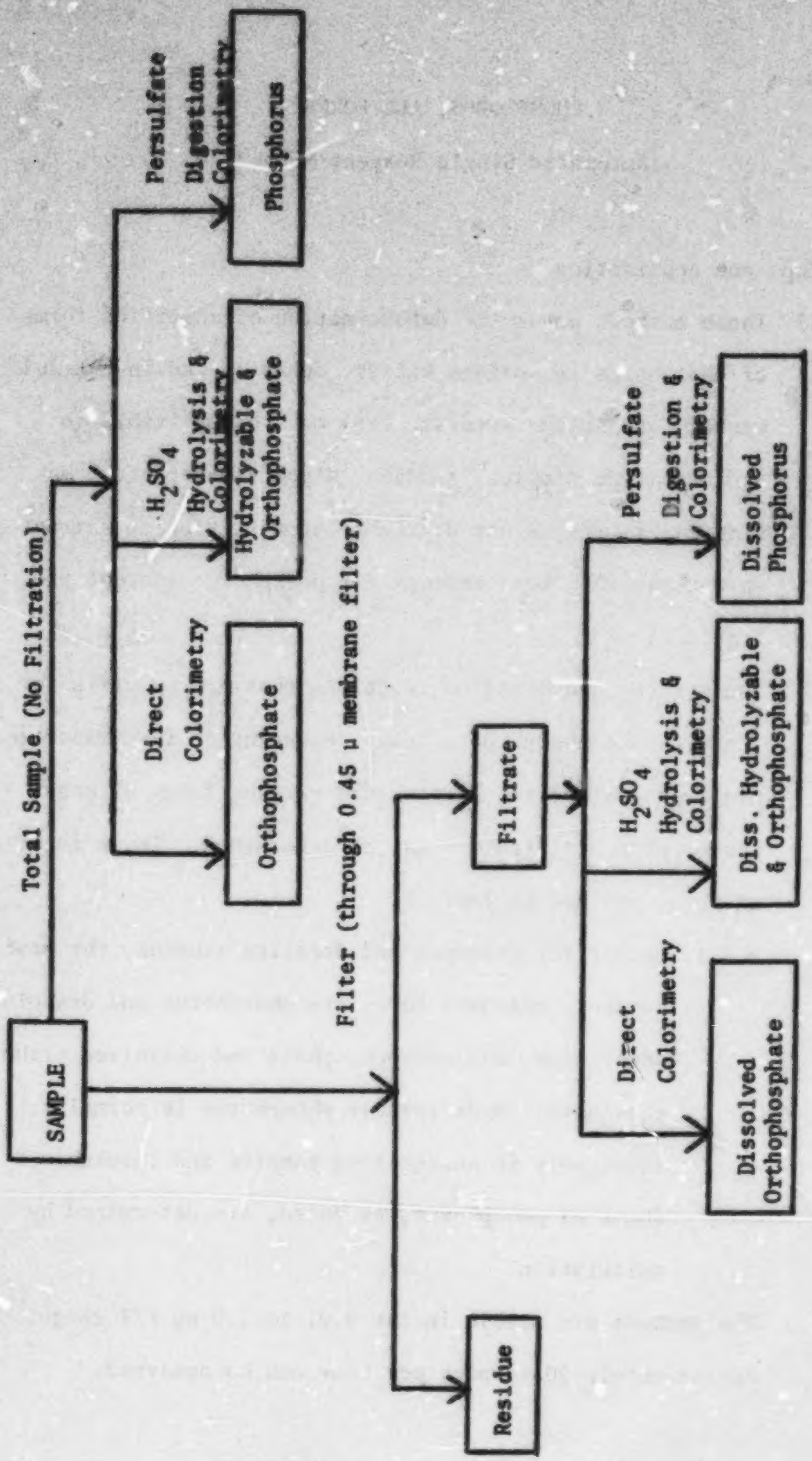

SAMPLE
Total Sample (No Filtration)
Direct Colorimetry
Orthophosphate
H_2SO_4 Hydrolysis & Colorimetry
Hydrolyzable & Orthophosphate
Persulfate Digestion Colorimetry
Phosphorus
Filter (through 0.45 μ membrane filter)
Filtrate
Residue
Direct Colorimetry
Dissolved Orthophosphate
H_2SO_4 Hydrolysis & Colorimetry
Diss. Hydrolyzable & Orthophosphate
Persulfate Digestion & Colorimetry
Dissolved Phosphorus

Figure 1. Analytical Scheme for Differentiation of Phosphorus Forms.

2. Summary of Method

2.1 Ammonium molybdate and potassium antimonyl tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phosphate-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.

2.2 Only orthophosphate forms a blue color in this test. Polyphosphates (and some organic phosphorus compounds) may be converted to the orthophosphate form by manual sulfuric-acid-hydrolysis. Organic phosphorus compounds may be converted to the orthophosphate form by manual persulfate digestion(2). The developed color is measured automatically on the AutoAnalyzer.

3. Definitions

3.1 The various forms of phosphorus are defined in Table 1.

4. Sample Handling and Preservation

4.1 If benthic deposits are present in the area being sampled, great care should be taken not to include these deposits.

4.2 Sample containers may be of plastic material, such as cubitainers, or of Pyrex glass.

4.3 If the analysis cannot be performed the same day of collection, the sample should be preserved by the addition of 40 mg $HgCl_2$ per liter and refrigeration at 4°C.

TABLE 1

PHOSPHORUS TERMINOLOGY

1. Phosphorus (P) - all of the phosphorus present in the sample regardless of form, as measured by the persulfate digestion procedure.
    a. Orthophosphate (P, ortho) - inorganic phosphorus $[(PO_4)^{-3}]$ in the sample as measured by the direct colorimetric analysis procedure.
    b. Hydrolyzable Phosphorus (P, hydro) - phosphorus in the sample as measured by the sulfuric acid hydrolysis procedure, and minus pre-determined orthophosphates. This hydrolyzable phosphorus includes polyphosphates $[(P_2O_7)^{-4}, (P_3O_{10})^{-5}$, etc.] + some organic phosphorus.
    c. Organic Phosphorus (P, org) - phosphorus (inorganic + oxidizable organic) in the sample as measured by the persulfate digestion procedure, and minus hydrolyzable phosphorus and orthophosphate.
2. Dissolved Phosphorus (P-D) - all of the phosphorus present in the filtrate of a sample filtered through a phosphorus-free filter of 0.45 micron pore size and measured by the persulfate digestion procedure.
    a. Dissolved Orthophosphate (P-D, ortho) - as measured by the direct colorimetric analysis procedure.

b. Dissolved Hydrolyzable Phosphorus (P-D, hydro) - as measured by the sulfuric acid hydrolysis procedure and minus pre-determined dissolved orthophosphates.

c. Dissolved Organic Phosphorus (P-D, org) - as measured by the persulfate digestion procedure, and minus dissolved hydrolyzable phosphorus and orthophosphate.

3. The following forms, when sufficient amounts of phosphorus are present in the sample to warrant such consideration, may be calculated:

   a. Insoluble Phosphorus (P-I) = (P) - (P-D).

      (1) Insoluble orthophosphate (P-I, ortho) = (P, ortho) - (P-D, ortho).

      (2) Insoluble Hydrolyzable Phosphorus (P-I, hydro) = (P, hydro) - (P-D, hydro).

      (3) Insoluble Organic Phosphorus (P-I, org) = (P, org) - (P-D, org).

4. All phosphorus forms shall be reported as P, mg/l.

5. Interferences

   5.1 It is reported(1) that no interference is caused by copper, iron, or silicate at concentrations many times greater than their greatest reported concentration in sea water. However, high iron concentrations can cause precipitation of phosphorus through the formation of clumps in the bottom of the sample.

   5.2 The salt error for samples ranging from 5 to 20 percent salt content was found to be less than 1 percent(1).

5.3 Arsenate, in concentrations greater than found in sea water, does not interfere(1).

6. Apparatus

6.1 Technicon AutoAnalyzer consisting of:

6.1.1 Sampler I

6.1.2 Manifold

6.1.3 Proportioning Pump

6.1.4 Heating Bath, 50°C

6.1.5 Colorimeter equipped with 50 mm tubular flow cell and 650 mμ filters

6.1.6 Recorder

6.2 Hot Plate or Autoclave

6.3 Acid-washed glassware: All glassware used in the determination should be washed with hot 1:1 HCl and rinsed with distilled water. The acid-washed glassware should be filled with distilled water and treated with all the reagents to remove the last traces of phosphorus that might be adsorbed on the glassware. Preferably, this glassware should be used only for the determination of phosphorus and after use it should be rinsed with distilled water and kept covered until needed again. If this is done, the treatment with 1:1 HCl and reagents is only required occasionally. Commercial detergents should never be used.

7. Reagents

7.1 Sulfuric acid solution, 5N: Dilute 70 ml of conc. H_2SO_4 with distilled water to 500 ml.

7.2 **Potassium antimonyl tartrate solution:** Weigh 0.3 g $K(SbO)C_4H_4O_6 \cdot 1/2\ H_2O$, dissolve in 50 ml distilled water in 100 ml volumetric flask, dilute to volume. Store in glass-stoppered bottle.

7.3 **Ammonium molybdate solution:** Dissolve 4 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 100 ml distilled water. Store in a plastic bottle at 4°C.

7.4 **Ascorbic acid, 0.1M:** Dissolve 1.8 g of ascorbic acid in 100 ml of distilled water. The solution is stable for about a week if stored at 4°C.

7.5 **Combined reagent:** Mix the above reagents in the following proportions for 100 ml of the mixed reagent: 50 ml of 5N H_2SO_4, 5 ml of potassium antimonyl tartrate solution, 15 ml of ammonium molybdate solution, and 30 ml of ascorbic acid solution. Mix after addition of each reagent. All reagents must reach room temperature before they are mixed and must be mixed in the order given. If turbidity forms in the combined reagent, shake and let it stand for a few minutes until the turbidity disappears before proceeding. This volume is sufficient for 4 hours operation. Since the stability of this solution is limited, it must be freshly prepared for each run.

7.6 **Strong-acid solution:** Slowly add 310 ml conc. H_2SO_4 to 600 ml distilled water. When cool, dilute to 1 liter.

7.7 **Ammonium persulfate.**

7. 8 **Wash water:** Add 40 ml of sulfuric acid solution to 1 liter of distilled water and dilute to 2 liters. (Not to be used when only orthophosphate is being determined.)

7. 9 Stock Solution: Dissolve 0.4393 g of pre-dried KH_2PO_4 in distilled water and dilute to 1 liter. 1 ml = 0.1 mg P.

7.10 Standard Solution A: Dilute 100 ml of stock solution to 1 liter. 1 ml = 0.01 mg P.

7.11 Standard Solution B: Dilute 100 ml of standard solution A to 1 liter. 1 ml = 0.001 mg P.

7.12 Prepare a series of standards by diluting suitable volumes of standard solutions A and B to 100.0 ml with distilled water. The following dilutions are suggested:

ml of Standard Solution B	Conc., mg P/l
0.0	0.00
2.0	0.02
5.0	0.05
10.0	0.10
ml of Standard Solution A	
2.0	0.20
5.0	0.50
8.0	0.80
10.0	1.00

Note: When the samples to be analyzed are saline waters, Substitue Ocean Water (SOW) should be used for preparing the standards; otherwise, distilled water is used. A tabulation of SOW composition follows:

NaCl	-	24.53g/l	$MgCl_2$	-	5.20g/l	Na_2SO_4	-	4.09g/l
$CaCl_2$	-	1.16g/l	KCl	-	0.70g/l	$NaHCO_3$	-	0.20g/l
KBr	-	0.10g/l	H_3BO_3	-	0.03g/l	$SrCl_2$	-	0.03g/l
NaF	-	0.003g/l						

8. Procedure

8.1 Phosphorus

8.1.1 Add 1 ml of strong-acid solution to a 50 ml sample in a 125-ml Erlenmeyer flask.

8.1.2 Add 0.4 gram of ammonium persulfate.

8.1.3 Boil gently on a pre-heated hot plate for approximately 30-40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15-20 psi).

8.1.4 Cool and dilute the sample to 50 ml.

8.1.5 Determine phosphorus as outlined in 8.3 Orthophosphate.

8.2 Hydrolyzable Phosphorus

8.2.1 Add 1 ml of strong-acid solution to a 50-ml sample in a 125-ml Erlenmeyer Flask.

8.2.2 Boil gently on a pre-heated hot plate for 30-40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15-20 psi).

8.2.3 Cool and dilute the sample to 50.0 ml.

8.2.4 The sample is now ready for determination of phosphorus as outlined in 8.3 Orthophosphate.

8.3 Orthophosphate

8.3.1 Set up manifold as shown in Figure 1.

8.3.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

8.3.3 Place wash water tubes (see 7.8) in Sampler, in sets of 2, leaving every third position vacant. Set sample timing at 1.0 minutes.

8.3.4 Place standards in Sampler in order of decreasing concentration. Complete filling of sampler tray with unknown samples.

8.3.5 Switch sample line from distilled water to Sampler and begin analysis.

9. Calculation

9.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentrations of samples by comparing sample peak heights with standard curve. Any sample whose computed value is less than 5% of its immediate predecessor must be rerun.

10. Precision and Accuracy

10.1 In a single laboratory, using surface water samples at concentrations of .04, 0.19, 0.35, and 0.84 mg P/l, standard deviations were ±0.005, ±0.000, ±0.003, and ±0.000, respectively (AQC Laboratory).

10.2 In a single laboratory, using surface water samples at concentrations of 0.07 and 0.76 mg P/1, recoveries were 99% and 100%, respectively (AQC Laboratory).

References

1. J. Murphy and J. Riley, "A Modified Single Solution Method for the Determination of Phosphate in Natural Waters." Anal. Chim. Acta., 27, 31 (1962).
2. M. Gales, Jr., E. Julian, and R. Kroner, "Method for Quantitative Determination of Total Phosphorus in Water." Jour AWWA, 58, No. 10, 1363 (1966).

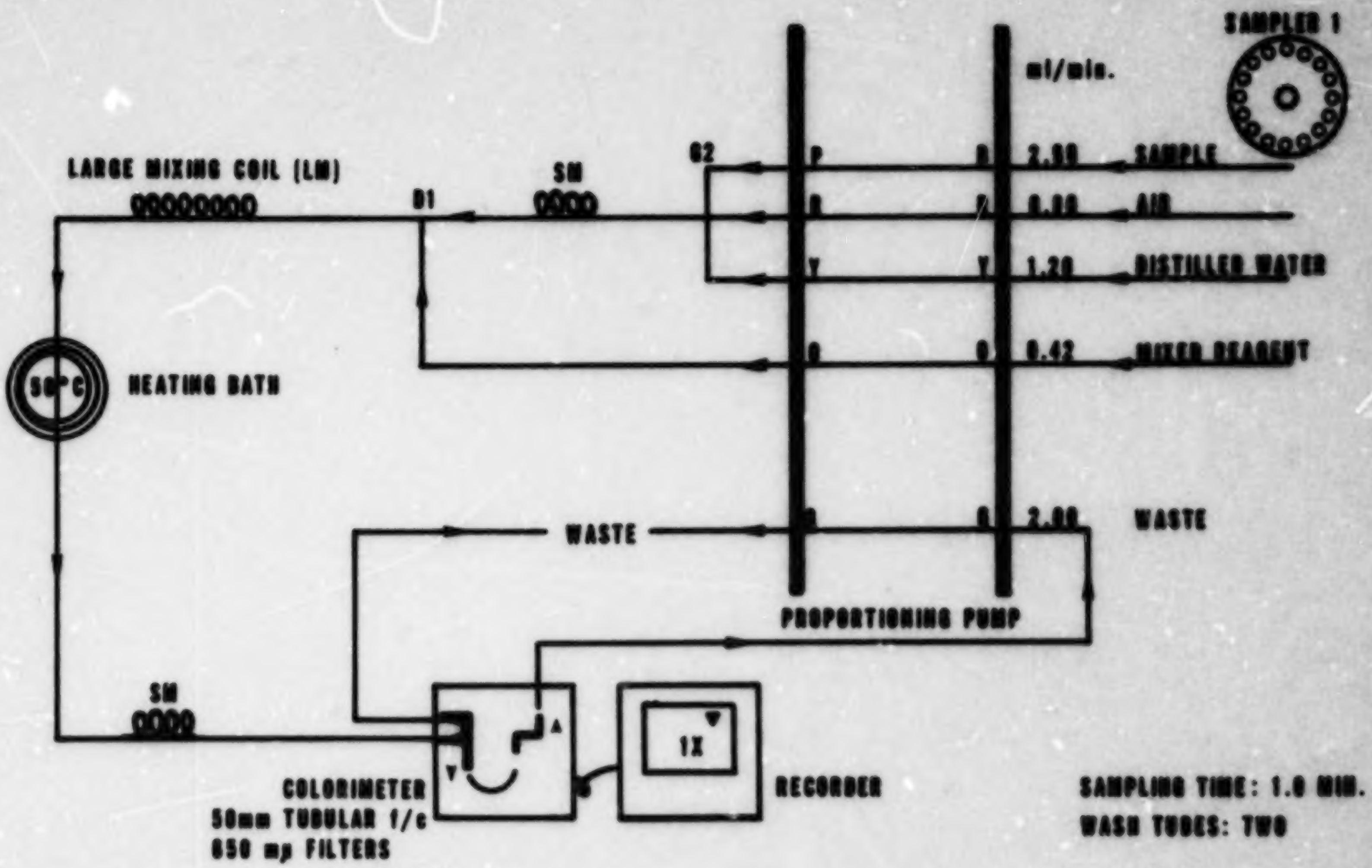

SAMPLER 1
ml/min.
P
B
2.00
SAMPLE
B
P
0.80
AIR
Y
Y
1.20
DISTILLED WATER
O
O
0.42
MIXED REAGENT
B
B
2.00
WASTE
G2
D1
SM
LARGE MIXING COIL (LM)
50°C
HEATING BATH
WASTE
PROPORTIONING PUMP
SM
COLORIMETER
50mm TUBULAR f/c
650 mμ FILTERS
1X
RECORDER
SAMPLING TIME: 1.0 MIN.
WASH TUBES: TWO

FIGURE 1. PHOSPHORUS SINGLE REAGENT MANIFOLD

Preceding page blank

PHOSPHORUS, ALL FORMS

(Automated Stannous Chloride Method)

1. Scope and Application

1.1 These methods cover the determination of specified forms of phosphorus in surface waters, domestic and industrial wastes. They may be applicable to sediment-type samples, sludges, algal blooms, etc., but sufficient data is not available at this time to warrant such usage when measurements for phosphorus content are required.

1.2 The methods are based on reactions that are specific for the orthophosphate ion. Thus, depending on the prescribed pre-treatment of the sample, the various forms of phosphorus given in Figure 1 may be determined. These forms are, in turn, defined in Table 1.

1.2.1 Except for in-depth and detailed studies, the most commonly measured forms are phosphorus and dissolved phosphorus, and orthophosphate and dissolved orthophosphate. Hydrolyzable phosphorus is normally found only in sewage-type samples and insoluble forms of phosphorus, as noted, are determined by calculation.

1.3 The methods are usable in the 0.01 to 1.0 mg P/l range. Approximately 15 samples per hour can be analyzed.

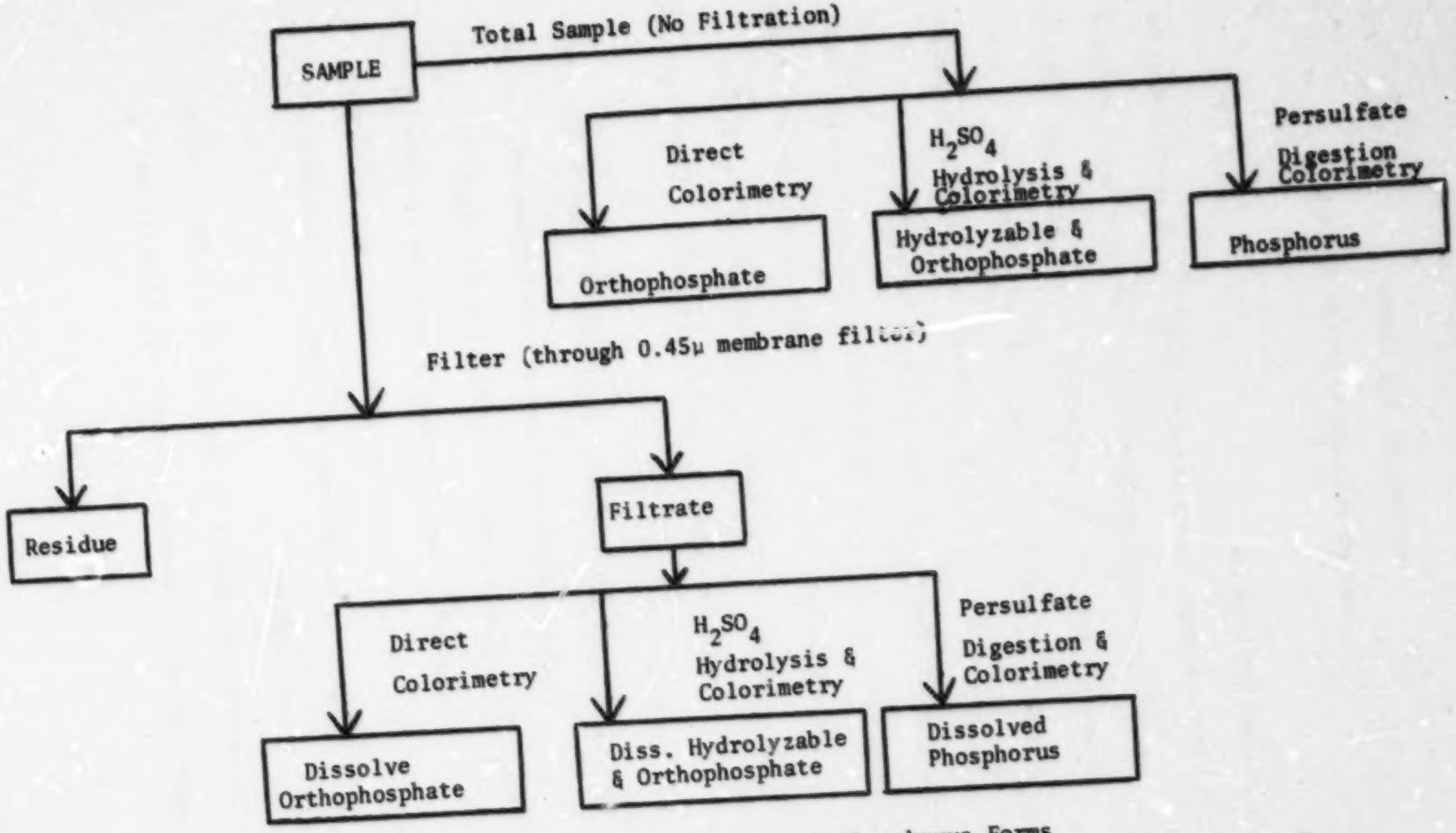

SAMPLE
Total Sample (No Filtration)
Direct
Colorimetry
Orthophosphate
H_2SO_4
Hydrolysis &
Colorimetry
Hydrolyzable &
Orthophosphate
Persulfate
Digestion
Colorimetry
Phosphorus
Filter (through 0.45μ membrane filter)
Residue
Filtrate
Direct
Colorimetry
Dissolve
Orthophosphate
H_2SO_4
Hydrolysis &
Colorimetry
Diss. Hydrolyzable
& Orthophosphate
Persulfate
Digestion &
Colorimetry
Dissolved
Phosphorus

Figure 1. Analytical Scheme for Differentiation of Phosphorus Forms

2. Summary of Method

2.1 Phosphorus is determined by manually digesting the samples with ammonium persulfate and sulfuric acid to convert the various forms of phosphorus to the orthophosphate form and measurement of this orthophosphate on the AutoAnalyzer.

2.2 In this colorimetric method, ammonium molybdate reacts with the orthophosphate in an acid medium to form a heteropoly acid, molybdophosphoric acid. This acid is reduced by stannous chloride to form the intensely colored complex, molybdenum blue, which is directly proportional to the amount of phosphorus.

3. Definitions

3.1 The various forms of phosphorus are defined in Table 1.

4. Sample Handling and Preservation

4.1 If benthic deposits are present in the area being sampled, great care should be taken not to include these deposits.

4.2 Sample containers may be of plastic material, such as cubitainers, or of Pyrex glass.

4.3 If the analysis cannot be performed the same day of collection, the sample should be preserved by the addition of 40 mg $HgCl_2$ per liter and refrigeration at 4° C.

5. Interferences

5.1 Method does not work on saline waters.

6. Apparatus

6.1 **Acid-washed glassware:** To prevent contamination, all glassware used in the preparation of standards and actual determinations should be washed with hot 1:1 HCl and rinsed with distilled water. The acid-washed glassware should be filled with distilled water and treated with all the reagents to remove the last traces of phosphorus that might be adsorbed on the glassware. Preferably, this glassware should be used only for the determination of phosphorus and after use it should be rinsed with distilled water and kept covered until needed again. If this is done, the treatment with 1:1 HCl and reagents is only required occasionally. Commercial detergents should never be used.

6.2 Technicon AutoAnalyzer consisting of:

6.2.1 Sampler I

6.2.2 Continuous Filter

6.2.3 Manifold

6.2.4 Proportioning Pump

6.2.5 Colorimeter equipped with 15 mm tubular flow cell and 650 mμ filters.

6.2.6 Recorder

6.3 Hot Plate or Autoclave

7. Reagents

7.1 Sulfuric acid solution: Cautiously add 310 ml of concentrated sulfuric acid slowly and with stirring to about 600 ml of distilled water. Cool and dilute to 1 liter.

7.2 Ammonium molybdate solution: Dissolve 12.5 g of $(NH_4)_6Mo_7O_{24}.4H_2O$ in 175 ml of distilled water. Cautiously add 77.5 ml of concentrated sulfuric acid slowly and with stirring to 400 ml of distilled water. Cool. Add the molybdate solution to the acid solution and dilute to 1 liter.

7.3 Stannous chloride solution: Dissolve 2.5 g of fresh $SnCl_2.2H_2O$ in 20 ml of hydrochloric acid. Warming on a hot plate will aid in dissolving this material. Dilute to 400 ml. Stable for 1 week at room temperature; one month at 4°C.

7.4 Wash water: Add 40 ml of sulfuric acid solution to 1 liter of distilled water and dilute to 2 liters.

7.5 Stock Solution: Dissolve 0.4393 g of pre-dried KH_2PO_4 in distilled water and dilute to 1 liter. 1 ml = 0.1 mg P.

7.6 Standard Solution A: Dilute 100 ml of stock solution to 1 liter. 1 ml = 0.01 mg P.

7.7 Standard Solution B: Dilute 100 ml of standard solution A to 1 liter. 1 ml = 0.001 mg P.

7.8 Prepare a series of standards by diluting suitable volumes of standard solutions A and B to 100.0 ml with distilled water. The following dilutions are suggested:

ml of Standard Solution B	Conc., mg P/l
1.0	0.01
2.0	0.02
5.0	0.05
10.0	0.10
ml of Standard Solution A	
2.0	0.20
5.0	0.50
8.0	0.80
10.0	1.00

7.9 Ammonium persulfate, reagent grade.

7.10 NaOH-EDTA solution: Dissolve 65 g NaOH and 6 g EDTA in distilled water and dilute to 1 liter.

8. Procedure

8.1 Phosphorus

8.1.1 Add 1 ml of sulfuric acid solution to a 50-ml sample in a 125-ml Erlenmeyer flask.

8.1.2 Add 0.4 g ammonium persulfate.

8.1.3 Boil gently on a pre-heated hot plate for approximately 30-40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15-20 psi).

8.1.4 Cool and dilute the sample to 50 ml.

8.1.5 The sample is now ready for automatic analysis as outlined in 8.3 Orthophosphate.

8.2 Hydrolyzable Phosphorus

8.2.1 Add 1 ml of sulfuric acid solution to a 50-ml sample in a 125-ml Erlenmeyer flask.

8.2.2 Boil gently on a pre-heated hot plate for approximately 30-40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15-20 psi).

8.2.3 Cool and dilute the sample to 50 ml.

8.2.4 The sample is now ready for automatic analysis as outlined in 8.3 Orthophosphate.

8.3 Orthophosphate

8.3.1 Set up manifold as shown in Figure 1.

8.3.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

8.3.3 Place wash water tubes (see 7.4) in alternate openings in Sampler and set sample timing at 2.0 minutes. Use distilled water, instead of acid-wash water when only orthophosphate is being determined.

8.3.4 Place standards in Sampler in order of decreasing concentration. Complete filling of sampler tray with unknown samples.

8.3.5 Switch sample line from distilled water to Sampler and begin analysis.

8.3.6 At end of run, clean out manifold system with NaOH-EDTA solution.

9. Calculation

9.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

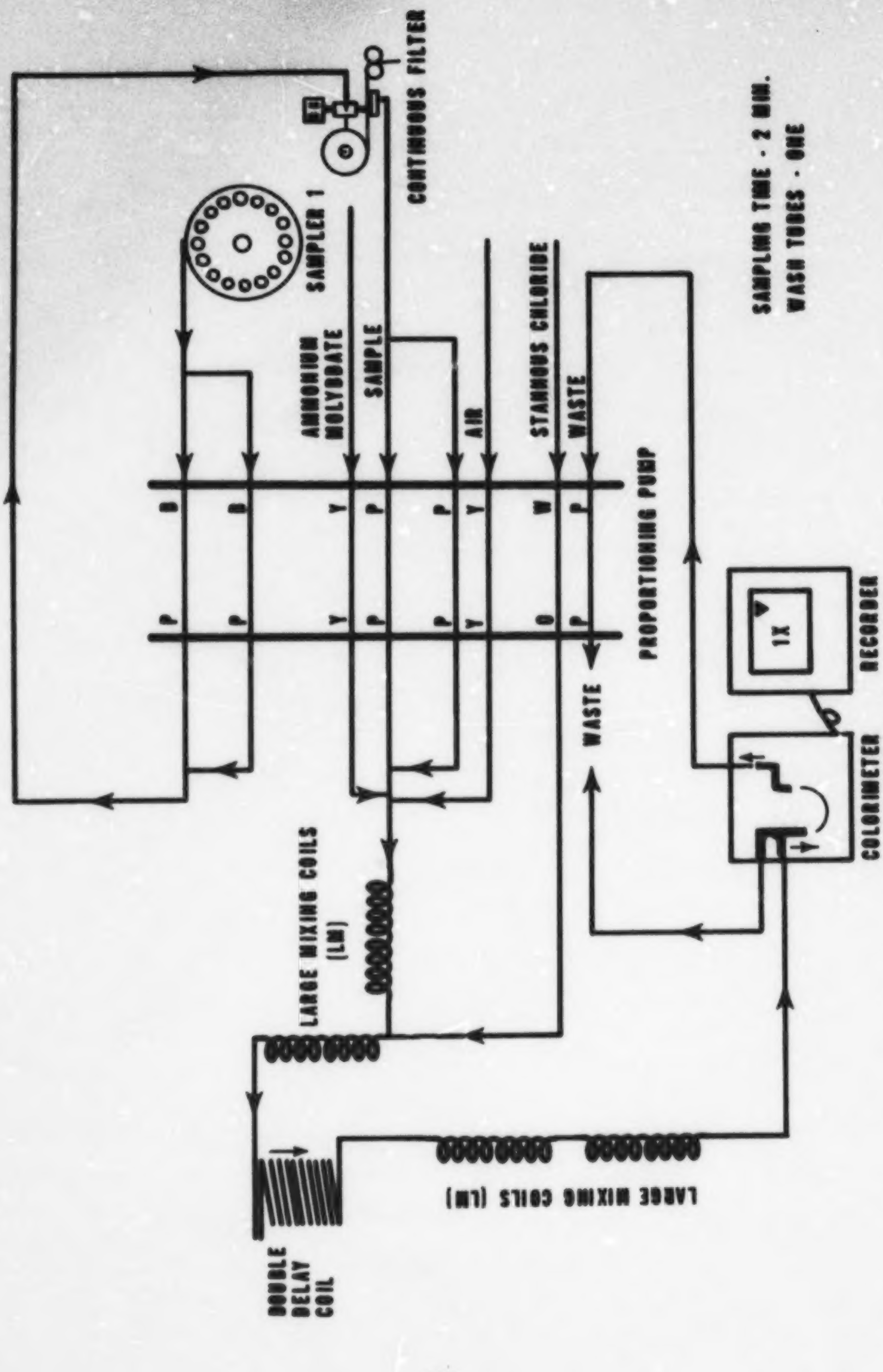
10. Precision and Accuracy

10.1 In a single laboratory, using surface water samples at concentrations of 0.06, 0.11, 0.48, and 0.62 mg P/1, the standard deviation was ±0.004 (AQC Laboratory).

10.2 In a single laboratory, using surface water samples at concentrations of 0.11 and 0.74 mg P/1, recoveries were 90% and 95%, respectively (AQC Laboratory).

References

1. Standard Methods for the Examination of Water and Wastewater, 12th Edition, p. 234, Amer. Pub. Health Asso., Inc., New York, N.Y. (1965).
2. M. Gales, Jr., E. Julian, and R. Kroner, "Method for Quantitative Determination of Total Phosphorus in Water." Jour. AWWA, 58, No. 10, 1363 (1966).


SAMPLER 1
CONTINUOUS FILTER
AMMONIUM MOLYBDATE
SAMPLE
AIR
STANNOUS CHLORIDE
WASTE
B
B
Y
P
P
Y
W
P
P
P
Y
P
P
Y
O
P
PROPORTIONING PUMP
WASTE
1X
RECORDER
COLORIMETER
15mm TUBULAR f/c
650 mμ FILTERS
LARGE MIXING COILS (LM)
LARGE MIXING COILS (LM)
DOUBLE DELAY COIL

SAMPLING TIME - 2 MIN.
WASH TUBES - ONE

FIGURE 1 - PHOSPHORUS MANIFOLD

SOLIDS, TOTAL

1. Scope and Application

1.1 This method is applicable to surface waters, domestic and industrial wastes, and saline waters.

1.2 The practical range of the determination is from 10 mg/l to 30,000 mg/l.

2. Summary of Method

2.1 A well mixed aliquot of the test sample is quantitatively transferred to a pre-weighed evaporating dish and evaporated to dryness at 103-105°C.

3. Definitions

3.1 Total Solids are defined as the sum of the homogenous suspended and dissolved materials in a sample.

4. Sample Handling and Preservation

4.1 No special precautions are required.

5. Interferences

5.1 Large, floating particles or submerged agglomerates (non-homogenous materials) should be excluded from the test sample.

5.2 Floating oil and grease, if present, should be included in the sample and dispersed by a blender device before aliquoting.

Preceding page blank

6. Apparatus

6.1 Evaporating Dishes, Porcelain, 90 mm, 100-ml capacity. (Vycor or platinum dishes may be substituted and smaller size dishes may be used if required.)

7. Procedure

7.1 Heat the clean evaporating dish to 550±50°C for 1 hour in a muffle furnace. Cool, dessicate, weigh and store in dessicator until ready for use.

7.2 Transfer a measured aliquot of sample to the pre-weighed dish and evaporate to dryness on a steam bath or in a drying oven.

7.2.1 Choose an aliquot of sample sufficient to contain a residue of at least 25 mg. To obtain a weighable residue, successive aliquots of sample may be added to the same dish.

7.2.2 If the evaporation is performed in a drying oven, the temperature should be lowered to approximately 98°C to prevent boiling and splattering of the sample.

7.3 Dry the evaporated sample for at least 1 hour at 103-105°C. Cool in a dessicator and weigh. Repeat the cycle of drying at 103-105°C, cooling, dessicating and weighing until a constant weight is obtained or until loss of weight is less than 4% of the previous weight, or 0.5 mg, whichever is less.

8. Calculation

8.1 Calculate total solids as follows:

$$\text{Total Solids, mg/l} = \frac{(\text{Wt. of sample + dish - wt. of dish})\ 1000}{\text{Vol. of Sample}}$$

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

SOLIDS, FILTERABLE

1. Scope and Application

1.1 This method is applicable to surface waters, domestic and industrial wastes, and saline waters.

1.2 The practical range of the determination is 10 mg/l to 20,000 mg/l.

2. Summary of Method

2.1 A well-mixed sample is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight at 180°C.

3. Definitions

3.1 Filterable solids are defined as those solids capable of passing through a standard glass fiber filter and dried to constant weight at 180°C.

4. Sample Handling and Preservation

4.1 No special precautions are required.

5. Interferences

5.1 Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying and dessication and quick weighing.

Preceding page blank

SOLIDS, FILTERABLE

1. Scope and Application

1.1 This method is applicable to surface waters, domestic and industrial wastes, and saline waters.

1.2 The practical range of the determination is 10 mg/l to 20,000 mg/l.

2. Summary of Method

2.1 A well-mixed sample is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight at 180°C.

3. Definitions

3.1 Filterable solids are defined as those solids capable of passing through a standard glass fiber filter and dried to constant weight at 180°C.

4. Sample Handling and Preservation

4.1 No special precautions are required.

5. Interferences

5.1 Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying and dessication and quick weighing.

Preceding page blank

5.2 Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180°C to insure that all the bicarbonate is converted to carbonate.

5.3 Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg.

6. Apparatus

6.1 Glass fiber filter discs, 4.7 cm or 2.2 cm, without organic binder, Reeve Angel type 984 H, Gelman type A, or equivalent.

6.2 Filter holder, membrane filter funnel or Gooch crucible adapter.

6.3 Suction flask, 500 ml.

6.4 Gooch crucibles, 25 ml (if 2.2 cm filter is used).

6.5 Evaporating dishes, porcelain, 100 ml. volume. (Vycor or platinum dishes may be substituted).

6.6 Steam bath.

6.7 Drying oven, 180°C±2°C.

6.8 Dessicator.

6.9 Analytical balance, 200 g capacity, capable of weighing to 0.1 mg.

7. Procedure

7.1 Preparation of glass fiber filter disc: Place the disc on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Remove filter from membrane filter apparatus or both crucible and filter if Gooch crucible is used, and dry in an oven at 103-105°C for one hour. Remove to dessicator and store until needed.

7.2 Preparation of evaporating dishes: Heat the clean dish to 550°C for one hour in a muffle furnace. Cool in dessicator and store until needed. Weigh immediately before use.

7.3 Assemble the filtering apparatus and begin suction. Shake the sample vigorously and rapidly transfer 100 ml to the funnel by means of a 100 ml volumetric cylinder. If suspended matter is low, a larger volume may be filtered.

7.4 Filter the sample through the glass fiber filter and continue to apply vacuum for about 3 minutes after filtration is complete to remove as much water as possible.

7.5 Transfer 100 ml (or a larger volume) of the filtrate to a weighed evaporating dish and evaporate to dryness on a steam bath.

7.6 Dry the evaporated sample for at least one hour at 180±2°C. Cool in a dessicator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 0.5 mg.

7.7 Note: The filtrate from the test for SOLIDS, NON-FILTERABLE, may be used for this determination.

8. **Calculation**

8.1 Calculate filterable solids as follows:

$$\text{Filt. solids, mg/l} = \frac{(\text{Wt. of dried residue} + \text{dish} - \text{wt. of dish}) \times 1000}{\text{Volume of filtrate used}}$$

9. **Precision and Accuracy**

9.1 Precision data are not available at this time.

9.2 Accuracy data on actual sample cannot be obtained.

SOLIDS, NON-FILTERABLE

1. Scope and Application

1.1 This method is applicable to surface waters, domestic and industrial wastes, and saline waters.

1.2 The practical range of the determination is 20 mg/l to 20,000 mg/l.

2. Summary of Method

2.1 A well-mixed sample is filtered through a standard glass fiber filter, and the residue retained on the filter is dried to constant weight at 103-105°C.

3. Definitions

3.1 Non-filterable solids are defined as those solids which are retained by a standard glass fiber filter and dried to constant weight at 103-105°C.

4. Sample Handling and Preservation

4.1 Non-homogenous particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample.

4.2 Preservation of the sample is not practical.

5. Interferences

5.1 Too much residue on the filter will entrap water and may require prolonged drying.

6. Apparatus

6.1 Glass fiber filter discs, 4.7 cm or 2.2 cm, without organic binder, Reeve Angel type 984 H, Gelman type A, or equivalent.

6.2 Filter holder, membrane filter funnel or Gooch crucible adapter.

6.3 Suction flask, 500 ml.

6.4 Gooch crucibles, 25 ml (if 2.2 cm filter is used).

6.5 Drying oven, 103-105°C.

6.6 Dessicator.

6.7 Analytical balance, 200 g capacity, capable of weighing to 0.1 mg.

7. Procedure

7.1 Preparation of glass fiber filter disc: Place the disc on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Remove filter from membrane filter apparatus or both crucible and filter if Gooch crucible is used, and dry in an oven at 103-105°C for one hour. Remove to dessicator and store until needed. Weigh immediately before use.

7.2 Assemble the filtering apparatus and begin suction. Shake the sample vigorously and rapidly transfer 100 ml to the funnel by means of a 100 ml volumetric cylinder. If suspended matter is low, a larger volume may be filtered.

7.3 Carefully remove the filter from the membrane filter funnel assembly. Alternatively, remove crucible and filter from crucible adapter. Place in drying oven and dry at 103-105°C to constant weight.

8. Calculations

8.1 Calculate non-filterable solids as follows:

$$\text{Non-filterable solids, mg/l} = \frac{(\text{Wt. of filter + residue - wt. of filter}) \times 1000}{\text{ml of sample filtered}}$$

9. Precision and Accuracy

9.1 Precision data are not available at this time.

9.2 Accuracy data on actual samples cannot be obtained.

SULFATE

(Automated Chloranilate Method)

1. Scope and Application

1.1 This automated method is applicable to surface waters, domestic and industrial wastes, and saline waters, in the range of 10 to 400 mg SO_4/1. Approximately 15 samples per hour can be analyzed.

2. Summary of Method

2.1 When solid barium chloranilate is added to a solution containing sulfate, barium sulfate is precipitated, releasing the highly colored acid chloranilate ion. The color intensity in the resulting chloranilic acid is proportional to the amount of sulfate present.

3. Sample Handling and Preservation

3.1 No special requirements.

4. Interferences

4.1 Cations, such as calcium, aluminum, and iron, interfere by precipitating the chloranilate. These ions are removed automatically by passage through an ion exchange column.

Preceding page blank

5. Apparatus

5.1 Technicon AutoAnalyzer consisting of:

5.1.1 Sampler I.

5.1.2 Continuous filter.

5.1.3 Manifold

5.1.4 Proportioning pump.

5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 520 mμ filters.

5.1.6 Recorder.

5.1.7 Heating bath, 45°C.

5.2 Magnetic stirrer.

6. Reagents

6.1 Barium chloranilate: Add 9 g of barium chloranilate ($BaC_6Cl_2O_4$) to 333 ml of ethyl alcohol and dilute to 1 liter with distilled water.

6.2 Acetate buffer, pH 4.63: Dissolve 13.6 g of sodium acetate in distilled water. Add 6.4 ml of acetic acid and dilute to 1 liter with distilled water. Make fresh weekly.

6.3 NaOH-EDTA Solution: Dissolve 65 g of NaOH and 6 g of EDTA in distilled water and dilute to 1 liter.

Note: This solution is also used to clean out manifold system at end of sampling run.

6.4 Ion Exchange Resin: Dowex-50 W-X8, ionic form $-H^+$.

Note: Column is prepared by sucking a solution of the resin into 12 inches of 3/16-inch OD sleeving. This may be conveniently done by using a pipette and a loose-fitting glass wool plug in the sleeve. The column, upon exhaustion, turns red.

6.5 Stock solution: Dissolve 1.4790 g of pre-dried Na_2SO_4 in distilled water and dilute to 1 liter. 1 ml = 1 mg.

6.5.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 ml with distilled water. The following dilutions are suggested:

ml of Stock Solution	Conc., mg/l
1.0	10
2.0	20
4.0	40
6.0	60
8.0	80
10.0	100
15.0	150
20.0	200
30.0	300
40.0	400

7. Procedure

7.1 Set up manifold as shown in Figure 1. (Note that any precipated $BaSO_4$ and the unused barium chloranilate are removed by filtration. If any $BaSO_4$ should come through the filter, it is complexed by the NaOH-EDTA reagent).

7.2 Allow both chlorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain suitable baseline.

7.3 Place distilled water wash tubes in alternate openings in sampler and set sample timing at 2.0 minutes.

7.4 Place working standards in sampler in order of decreasing concentration. Complete filling of sampler tray with unknown samples.

7.5 Switch sample line from distilled water to sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (AQC), using surface water samples at concentrations of 39, 111, 188, and 294 mg SO_4/1, the standard deviations were ±0.6, ±1.0, ±2.2, and ±0.8, respectively.

9.2 In a single laboratory (AQC) using surface water samples at concentrations of 82 and 295 mg SO_4/1, recoveries were 99% and 102%, respectively.

Reference

1. R. J. Bertolocini and J. E. Barney, Anal. Chem., 29, 283 (1957).

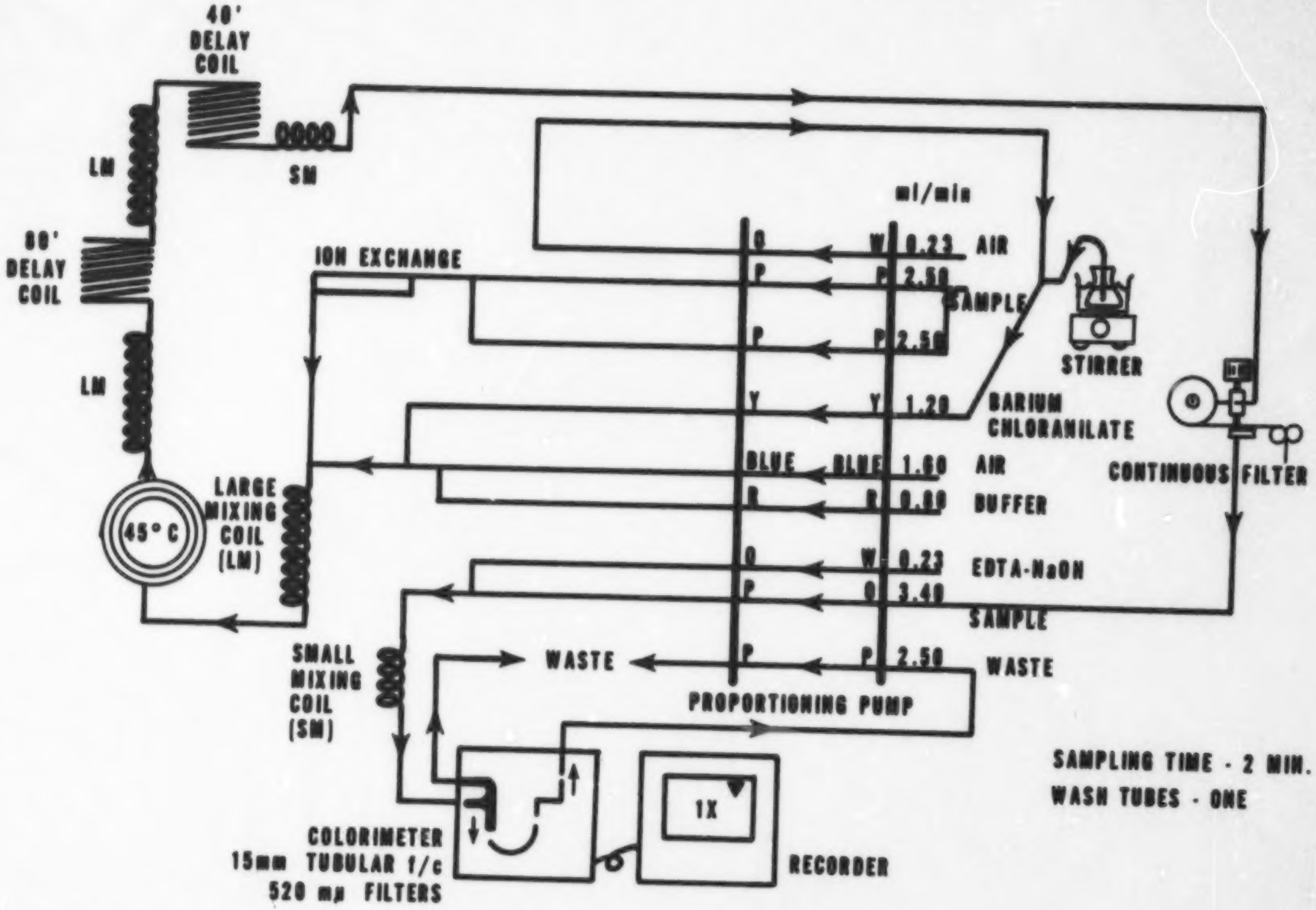

40' DELAY COIL
SM
LM
80' DELAY COIL
LM
45° C
LARGE MIXING COIL (LM)
ION EXCHANGE
ml/min
O
W
0.23
AIR
P
P
2.50
SAMPLE
P
P
2.50
STIRRER
Y
Y
1.20
BARIUM CHLORANILATE
BLUE
BLUE
1.60
AIR
R
R
0.80
BUFFER
CONTINUOUS FILTER
O
W
0.23
EDTA-NaOH
P
O
3.40
SAMPLE
P
P
2.50
WASTE
WASTE
PROPORTIONING PUMP
SMALL MIXING COIL (SM)
1X
COLORIMETER 15mm TUBULAR f/c 520 mμ FILTERS
RECORDER
SAMPLING TIME - 2 MIN.
WASH TUBES - ONE

FIGURE 1 - SULFATE MANIFOLD

TURBIDITY

1. Scope and Application

1.1 This method is applicable to surface and saline waters in the range of turbidity from 0 to 40 Jackson units.

2. Summary of Method

2.1 The method is based upon a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension. The higher the intensity of scattered light, the higher the turbidity. Readings, in Jackson units, are made in a nephelometer designed according to specifications outlined in Apparatus, 5. A standard suspension of Formazin, also prepared under closely defined conditions, is used to calibrate the instrument.

2.1.1 Formazin polymer is used as the turbidity reference suspension for water because it is more reproducible than other types of standards previously used for turbidity standards.

3. Sample Handling and Preservation

3.1 Samples taken for turbidity measurements should be analyzed as soon as possible. Preservation of samples is not recommended.

4. Interferences

4.1 The presence of floating debris and coarse sediments which settle out rapidly will give false high readings. Finely divided air bubbles will also affect the results in a positive manner.

4.2 The presence of true color, that is the color of water which is due to dissolved substances which absorb light will cause turbidities to be low, although this effect is generally not significant with finished waters.

5. Apparatus

5.1 The turbidimeter shall consist of a nephelometer with light source for illuminating the sample and one or more photoelectric detector with a readout device to indicate the intensity of light scattered at right angles to the path of the incident light. The turbidimeter should be so designed that little stray light reaches the detector in the absence of turbidity and should be free from significant drift after a short warm-up period.

5.2 The sensitivity of the instrument should permit detection of turbidity differences of 0.02 unit or less in waters having turbidities less than 1 unit. The instrument should measure from 0 to 40 units turbidity. Several ranges will be necessary to obtain both adequate coverage and sufficient sensitivity for low turbidities.

5.3 The sample tubes to be used with the available instrument must be of clear, colorless glass. They should be kept scrupulously clean, both inside and out, and discarded when they become scratched or etched. They must not be handled at all where the light strikes them, but should be provided with sufficient extra length, or with a protective case, so that they may be handled.

5.4 Differences in physical design of turbidimeters will cause differences in measured values for turbidity even though the same suspension is used for calibration. To minimize such differences, the following design criteria should be observed:

5.4.1 Light source: Tungsten lamp operated at not less than 85% of rated voltage or more than rated voltage.

5.4.2 Distance traversed by incident light and scattered light within the sample tube: Total not to exceed 10 cm.

5.4.3 Angle of light acceptance of the detector: Centered at 90° to the incident light path and not to exceed ±30° from 90°.

5.4.4 Maximum turbidity to be measured: 40 units.

5.5 At the time of this writing, the only instrument commercially available with these specifications is the Hach Turbidimeter, Model 3100. This instrument is recommended.

6. Reagents

6.1 Turbidity-free water - Pass distilled water through a 0.45 μ pore size membrane filter if such filter and water shows a lower turbidity than the distilled water.

6.2 Stock turbidity suspension:

Solution 1: Dissolve 1.00g hydrazine sulfate, $(HN_2)_2.H_2SO_4$, in distilled water and dilute to 100 ml in a volumetric flask.

Solution 2: Dissolve 10.00g hexamethylenetetramine in distilled water and dilute to 100 ml in a volumetric flask.

In a 100-ml volumetric flask, mix 5.0 ml Solution 1 with 5.0 ml Solution 2. Allow to stand 24 hours at 25 ± 3°C, then dilute to the mark and mix.

6.3 Standard turbidity suspension: Dilute 10.00 ml stock turbidity suspension to 100 ml with turbidity-free water. The turbidity of this suspension is defined as 40 units. Dilute portions of the standard turbidity suspension with turbidity-free water as required.

6.3.1 A new stock turbidity suspension should be prepared each month. The standard turbidity suspension and dilute turbidity standards should be prepared weekly by dilution of the stock turbidity suspension.

7. Procedure

7.1 Turbidimeter calibration: The manufacturer's operating instructions should be followed. Measure standards on the turbidimeter covering the range of interest. If the instrument is already calibrated in standard turbidity units, this procedure will check the accuracy of the calibration scales. At least one standard should be run in each instrument range to be used. Some instruments permit adjustment of sensitivity so that scale values will correspond to turbidities.

Reliance on a manufacturer's solid scattering standard for setting overall instrument sensitivity for all ranges is not an acceptable practice unless the turbidimeter has been shown to be free of drift on all ranges. If a pre-calibrated scale is not supplied, then calibration curves should be prepared for each range of the instrument.

7.2 Turbidities less than 40 units: Shake the sample to thoroughly disperse the solids. Wait until air bubbles disappear then pour the sample into the turbidimeter tube. Read the turbidity directly from the instrument scale or from the appropriate calibration curve.

7.3 Turbidities exceeding 40 units: Dilute the sample with one or more volumes of turbidity-free water until the turbidity falls below 40 units. The turbidity of the original sample is then computed from the turbidity of the diluted sample and the dilution factor. For example, if 5 volumes of turbidity-free water were added to 1 volume of sample, and the diluted sample showed a turbidity of 30 units, then the turbidity of the original sample was 180 units.

7.3.1 The Hach Turbidimeter, Model 2100, is equipped with 5 separate scales: 0-.02, 0-1.0, 0-10.0, 0-100, and

0-1000 JTU. It is strongly recommended, however, that the upper scales be used as indications of required dilution volumes to reduce readings to less than 40 JTU. (NOTE: Comparative work performed in the AQC Laboratory indicates a progressive error on sample turbidities in excess of 40 units.)

8. Calculation

8.1 Multiply sample reading by appropriate dilution to obtain final reading.

8.2 Report results as follows:

Jackson Turbidity Units	Record to nearest:
0.0-1.0	0.05
1-10	0.1
10-40	1
40-100	5
100-400	10
400-1000	50
>1000	100

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.